TEXTILE ANALYSIS.

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PREFACE.

ONE of the authors of this book has conducted a class in Advanced Textile Technology for some years in University College, Nottingham, and the book is based upon notes drawn up for this class. Most of the subjects with which Textile Chemists have to deal have been included, and numerous references have been made to Scientific Journals. Many of the problems which a Textile Chemist has to solve partake of the nature of research work. Although these problems cannot be solved by analysis alone, a knowledge of the analytical methods usually employed is always necessary.

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TEXTILE ANALYSIS.

CHAPTER I.

THE IDENTIFICATION AND DETERMINATION OF TEXTILE FIBRES.

SINCE the fibres are the most important raw materials with which the textile chemist must deal, it is natural that their identification and determination should be considered first. Those fibres which find application in the textile trade can be classified in the following manner:

Group I.—Animal Fibres.

Sub-group (a)—Appendages of the Epidermis. Including wool, alpaca, mohair and rabbit fur.

Sub-group (b)—Animal Secretions. The various forms of silk are the only ones of importance.

Group II.—Vegetable Fibres.

Sub-group (a)—Unicellular Fibres. Cotton and kapok.

Sub-group (b)—Multicellular Vegetable Fibres. This class includes ramie, flax, jute and hemp.

Group III.—Artificial Vegetable Fibres. Including all commercial varieties of artificial silk and also the staple fibres from artificial silk which go under the name of artificial wool.

Group IV.—Mineral Fibres. Asbestos and glass.

There is little difficulty as a rule in deciding upon the group to which a fibre belongs when only one is being dealt with, but when a fabric contains two or more fibres the problem is not always easy. When it is a question of distinguishing between the different members of the same group, almost insurmountable difficulties may be encountered.

Microscopic Examination.—A microscopic examination should be made first. The sample should be degreased by washing with petroleum ether or benzene and, if it be highly discoloured, it should be bleached. A dilute solution of hydrogen peroxide (2 vols.) made faintly alkaline with ammonia is a suitable bleaching agent, or a one per cent. solution of potassium permanganate in the presence of dilute sulphuric acid, decolorised afterwards with sulphurous acid. Very often dyed samples will not strip with the oxidising bleaching agents mentioned above; in such cases a solution of sodium hydrosulphite made alkaline with ammonia should be used, or, in the case of cotton, a solution of sodium hypochlorite of about 1° Tw. (2·7 grms. chlorine per litre) may be substituted. Hypochlorite must, however, never be used for wool, as it tends

to alter the microscopic appearance of the fibre. Titanous chloride is a very powerful stripping agent for dyed materials. A little of the prepared sample is then teased out and mounted in water for examination. Unless a permanent slide is required, water is the best mounting agent for all textile fibres except artificial silks. Lawrie (*J. Soc. Dyers and Col.*, 1928, 73) states that artificial silks show their characteristic markings to the best advantage when mounted in the following manner: The fibres are first dehydrated by immersing them successively in alcohol of 25, 50, 75 and 100 per cent. concentrations; they should remain in the first three solutions for about two hours, and then for four hours in the 100 per cent. alcohol. It is advisable to clear them by two immersions in xylene, cedar wood oil, oil of Bergamot or synthetic oil of winter-green. They are then mounted in glycerine jelly or castor oil. Canada balsam should not be used since its refractive index is too near that of the artificial silks.

A slide for microscopic examination prepared in the manner described is often insufficient for the identification of a fibre, particularly in the case of artificial silks. When further information is required, a cross-section should be examined as well as the appearance of the fibre when mounted in the usual manner as just described. According to Lawrie (*loc. cit.*), *Celloidin*, which is a pure collodion, is the best material to use in the preparation of the sections, since it need not be removed afterwards, the sections being mounted directly in euparal or glycerine jelly; the fibres are drawn until they are parallel to one another, wrapped round a wire frame and immersed for an hour in a solution of *Celloidin* in equal parts of alcohol and ether. They are then removed and the *Celloidin* is coagulated by means of chloroform or by drying in air. The preparation is then placed in pith and sections are cut with a sharp razor. A microtome may be used but, if so, should not be of the rocking type. Paraffin or a solution of cellulose acetate in chloroform may be used instead of *Celloidin*, but in both cases the cross-sections must be dissolved out before they can be mounted for microscopic examination.

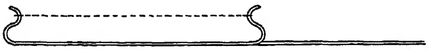


Fig. 1.—Wire Frame for Supporting Fibre.

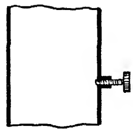


Fig. 2.—Brass Tube for Waxing.

The cutting of cross-sections of textile fibres is described by W. Garner (*J. Soc. Dyers and Col.*, 1926, 269). The fibre is supported on a small wire frame such as is shown in fig. 1 and is soaked in filtered beeswax at 100° C. for a few minutes to remove all air bubbles. It is then placed in a brass tube with a screw adjustment (fig. 2) and molten paraffin wax poured in. The object of the screw adjustment is to avoid loose embedding of the fibre owing to contraction of the wax on cooling. When the wax has set it is removed from the mould and a pencil is cut out separating the embedded fibre from the wire. Sections are then cut on a microtome.

To mount the sections, a clean slide is rubbed with a 1 per cent. solution of gelatin and the wax containing the cross-section is laid on the slide. The slide is then dried in an oven, allowed to cool and placed in petroleum ether during one hour to dissolve the wax. The section adheres to the slide owing to the presence of the gelatin. It is then mounted in glycerine jelly.

Clegg and Harland (*Shirley Inst. Mem.*, Vol. II., 1923, 353, and *J. Soc. Dyers and Col.*, 1924, 55) described the following procedure for cotton: Fibres

in a bundle are drawn out parallel, mounted on a wire frame and immersed in alcohol for two minutes to drive out air bubbles, then being transferred to water. A gelatin solution, which shall be quite stiff when cold, is melted on a water-bath and the frame is completely immersed in it. The frame and gelatin are allowed to stand in an oven for three hours, at such a temperature that the gelatin remains liquid, after which the frame is immersed in a mixture of 5 per cent. formalin (40 per cent.) and 95 per cent. alcohol in order to harden the gelatin adhering to the cotton. The frame is left in the hardening solution for several hours, preferably over-night, and is finally placed in absolute alcohol for five minutes to complete the hardening. The cotton is then cut away from the frame and mounted in vaseline-paraffin, the sections cut with a hand microtome and finally mounted in glycerin jelly.

A quick method of preparing sections of textile fibres is described by Schwartz (*Amer. Dyestuffs Rep.*, 1928, **17**, 261-6). The specimen is dried for a few minutes in the usual textile conditioning or drying oven or simpler substitute, and immersed in paraffin. It is then removed slowly and dipped in ice-water, the process being repeated until a small "candle" about $\frac{1}{4}$ inch in diameter is built up. A piece is cut off and fixed to the top of a thin rod to facilitate handling. After thorough hardening in ice-water, thin sections are cut with a new safety razor blade of the wafer type. The sections are placed on the slide and the outer rings of paraffin removed. The slide is then warmed just enough to stick the sections to it firmly without melting them in the least. Drops of the desired dye are placed on each section and the excess removed with filter paper.

Preliminary Sorting Tests.—There are certain simple preliminary tests which are useful in the examination of fibres; these are (1) the burning test, (2) the heating test, (3) the caustic soda test.

Vegetable fibres ignite readily and burn freely, without the production of fumes or smell. Animal fibres do not ignite so readily as vegetable fibres and when burning frizzle, forming a brownish semi-liquid mass, giving off at the same time fumes which have the characteristic odour of burning feathers. Weighted silk is, however, often practically incombustible, but when held in a Bunsen flame, is reduced gradually to an ash which retains the form of the original thread. An artificial silk is generally recognisable by its appearance, but it may be noted that regenerated cellulose varieties burn just like cotton, and acetate silk fuses and forms globules. When vegetable fibres are heated in a test tube, they give off acid fumes, leaving a residue of charcoal. When animal fibres are treated in the same way, ammonia is evolved, and in the case of wool, sulphuretted hydrogen also. All animal fibres dissolve in a boiling 5 per cent. solution of sodium hydroxide; vegetable fibres do not. This test is useful where two or more different fibres are present. The solutions obtained when wool, hair or fur is dissolved in sodium hydroxide contain sodium sulphide, which gives a black precipitate of lead sulphide with lead acetate solution.

When there is any doubt about the presence of an animal fibre, such as might arise in the case of a fine filament of cuprammonium yarn containing a small proportion of real silk, where microscopic examination would be of little use, it is advisable to test for nitrogen. A small piece of the fabric is ignited with sodium in a test tube, the products are dissolved in water and the solution filtered. A crystal of ferrous sulphate is added to the filtrate, which must be alkaline, and if necessary, should have sodium hydroxide added, and the liquid is heated to the boiling point. Hydrochloric acid is then added in excess, and if the solution then has a blue colour, an animal fibre is present. The test is very delicate, but a dyed sample must be stripped first, since the nitrogen in the

dyestuff would be sufficient to give a faint reaction. Wool and silk can be distinguished, in the absence of dyestuffs, by testing for sulphur. If the alkaline solution after fusion with sodium gives a deep purple colour with sodium nitroprusside, sulphur is present, indicating the presence of wool or an allied hair. If, on the other hand, nitrogen is found but not sulphur, it shows that the only animal fibre which the sample contained was silk.

GROUP TESTS.

There are some general reactions by which the different groups may be distinguished from one another, but these are not so reliable as a microscopic examination. The common group reagents are (*a*) concentrated sulphuric acid, (*b*) concentrated hydrochloric acid, (*c*) 5 per cent. sodium hydroxide solution, (*d*) Loewe's reagent, (*e*) Richardson's reagent.

Loewe's Reagent is made by dissolving 10 grms. of copper sulphate in 100 c.c. of water, adding 5 grms. of glycerol and then sufficient concentrated sodium hydroxide just to dissolve the precipitate which is first formed.

Richardson's Reagent, or ammoniacal nickel oxide solution, is made by dissolving 5 grms. of nickel sulphate in water and treating with a slight excess of sodium hydroxide. The nickel hydroxide is filtered off, washed until free from alkali and dissolved in 50 per cent. aqueous ammonia solution.

In using these two solutions gentle warming accelerates the action.

Group I.

Sub-group (a).

Concentrated sulphuric acid dissolves wool, hair and fur slowly, but hydrochloric acid does not. Neither Loewe's nor Richardson's reagent has any solvent action, but a boiling 5 per cent. solution of sodium hydroxide dissolves members of the group, and the solution gives a black precipitate with lead acetate and a purple coloration with sodium nitroprusside.

Sub-groub (b).

Silk dissolves slowly in cold concentrated sulphuric acid or hydrochloric acid. When warmed gently with hydrochloric acid it dissolves completely in a few minutes. A boiling 5 per cent. solution of sodium hydroxide dissolves silk and the solution gives no reaction for sulphides. Both Loewe's and Richardson's reagents dissolve silk slowly when cold, but quickly when warm.

Group II.

Sub-group (a).

Cotton dissolves in cold concentrated sulphuric acid, and if the solution be poured at once into excess of cold water, a precipitate of amyloid is formed. When cotton is heated with sulphuric acid, charring takes place, as with other carbohydrates. Ordinary concentrated cold hydrochloric acid does not dissolve cotton, nor does cold or hot sodium hydroxide solution, Loewe's or Richardson's reagent.

Sub-group (b).

Cold concentrated sulphuric acid dissolves multicellular fibres, but more slowly than it does cotton. The results with the other reagents are the same as with cotton.

Group III.

Artificial silks dissolve in concentrated sulphuric acid, and if they are regenerated celluloses, swell up with hydrochloric acid. Five per cent. sodium hydroxide solution also produces considerable swelling, accompanied by partial solution. No visible change occurs when artificial silks are treated with Loewe's or Richardson's reagent.

Group IV.

None of the reagents mentioned has any effect on mineral fibres.

THE DISTINCTION OF DIFFERENT MEMBERS OF THE SAME GROUP.

Group I.

Sub-group (a).

There is no chemical method of distinguishing between the different types of wool or hair. Very careful microscopic examination must be resorted to and comparisons made with definite samples of wool, mohair, alpaca or whatever hair is suspected.

Sub-group (b).

The only member of this group which has any commercial importance is silk from *Bombyx mori* and wild or Tussur silk. The latter, on account of the resistance which it offers to bleaching, is generally met with in its unbleached state and has a light buff colour. Its micro-structure differs from that of true silk: the fibre is coarser, has longitudinal striations and a natural twist. Tussur silk differs also from true silk in its greater resistance to the action of acids, alkalis and solvents, as may be seen from the following table:

	True Silk.	Tussur Silk.
Boiling 1 per cent. sodium hydroxide,	Dissolved rapidly.	Dissolved in 30 to 50 minutes.
Cold hydrochloric acid, sp. gr. 1·16, .	Do.	Dissolves very slowly.
Zinc chloride solution, . . .	Do.	Do.

Group II.

Sub-group (a).

From a chemical point of view kapok differs from cotton in that it contains lignocellulose and hence is stained yellow when soaked in an aqueous solution of aniline sulphate and crimson by phloroglucinol. For the latter test a 10 per cent. alcoholic solution of phloroglucinol is mixed with an equal volume of 10 per cent. hydrochloric acid just before use; a little of the sample is soaked in this solution and then steamed on the water bath.

Lejeune (*J. Soc. Dyers and Col.*, 1926, 232) gives the following tests also: (*a*) After immersion in a solution of 5 per cent. of iodine in 10 per cent.

potassium iodide, followed by steeping in a cold solution of sulphuric acid, water and glycerine (4 : 1 : 1 by volume), cotton is coloured blue-black and kapok yellowish-brown. (*b*) Since basic triphenylmethane colours have a selective preference for kapok, it is possible to distinguish between this fibre and cotton in a mixture by placing the material in a boiling neutral solution of Malachite Green, followed by immersion in a slightly ammoniacal bath of Oxamine Red at about 99° C. Under these conditions kapok is stained dark green and cotton bright red and an approximate determination of their proportions is practicable.

Raw and Bleached Cotton.—Raw cotton differs from bleached or dye-boiled cotton in being difficult to wet. It also has a greater affinity for both basic and acidic dyestuffs, but does not dye readily with direct dyestuffs in a cold bath. Sieber (*Textilber*, 1928, 404) gives the following test: 0·1 grm. of the sample is immersed for 30 to 60 seconds in 10 c.c. of a boiling solution of Victoria Blue B, containing 3 per cent. of the dyestuff on the weight of the sample. The cotton is then washed with cold water, immersed for one minute in boiling water, washed again with cold water and dried. Raw cotton fibres are coloured uniformly ; bleached fibres are only slightly stained, the linen remaining uncoloured.

Mercerised Cotton.—Fully mercerised cotton consists of cylindrical hairs practically devoid of twist.

Chemical Tests : The following are the chief tests for distinguishing between mercerised cotton and unmercerised cotton :—

Lange's Test: For this, two solutions are required, viz., (*a*) 5 grms. of potassium iodide and 1 grm. of iodine dissolved in 16 c.c. of water ; (*b*) 25 grms. of zinc chloride dissolved in 12 c.c. of water. These solutions are mixed, allowed to settle and the clear liquid drawn off. The sample is soaked in the reagent for 3 minutes. Both mercerised and unmercerised cotton are stained brown. The stained samples are washed with boiled and cooled distilled water until the brown colour due to the excess of iodine has given place to dark blue-black. The samples are now placed in fresh water. Ordinary cotton becomes decolorised rapidly, whilst in the case of mercerised cotton the bluish colour persists for some time. The results given by this test are not reliable in the presence of oxycellulose.

Knecht's Test: The sample is boiled for thirty minutes in a 0·5 per cent. solution of benzopurpurin, a similar test being made with a piece of unmercerised cotton. The dyed samples are washed and dried. If all the conditions are the same, the mercerised cotton will be dyed more deeply than the unmercerised sample. If the amount of dyestuff taken up is determined by titration with titanous chloride solution, the degree of mercerisation may be estimated. Knecht found that fully dyed unmercerised cotton takes up 1·77 per cent. of benzopurpurin, whilst completely mercerised cotton takes up 3·60 per cent.

David's Test: This is useful for fabrics. The material is spotted with strong sodium hydroxide solution and after ten minutes washed and dyed with benzopurpurin. If unmercerised or incompletely mercerised, the spotted portions will be dyed more deeply than the rest of the sample.

Kinkead's Test: The sample is stained by soaking it for a few minutes in a 0·001 per cent. solution of Methylene Blue containing 0·5 per cent. of sodium carbonate. It is then rinsed with water, placed in a fresh test tube and covered with 10 c.c. of a 3 per cent. solution of sodium carbonate. Four drops of a solution of 1 grm. of iodine dissolved in 100 c.c. of 20 per cent. potassium iodide are added and the contents of the tube heated to the boiling-point. The boiling liquid is poured off and replaced immediately by cold 3 per cent. sodium carbonate solution. Mercerised cotton becomes reddish-purple in colour,

unmercerised cotton acquiring a blue or greenish tint according to the degree of mercerisation. Thus :—

Strength of Caustic Soda Used in Mercerising.	Colour.
Nil.	Bright Blue or Greenish-blue.
20° Tw.	Slightly Red.
30° Tw.	Distinctly Red.
40°-50° Tw.	Full Purple.
60°-70° Tw.	Rather Bluer than with 40°-50° Tw.

Knecht and Knagg's Test : Unmercerised cotton dyed with benzopurpurin becomes blue when treated with hydrochloric acid ; mercerised cotton remains red or reddish-violet unless excess of acid is present. The test is carried out by dyeing the sample together with a little unmercerised cotton with benzopurpurin, placing the dyed samples in a beaker containing water and adding dilute hydrochloric acid drop by drop until the unmercerised cotton turns blue. The test sample if mercerised will remain unchanged.

Hübner's Test (*J. S. C. I.*, 1908, 105) : When mercerised cotton is soaked in zinc chloriodide solution it becomes stained, the colour produced depending upon the degree of mercerisation. Unmercerised cotton on the other hand is not stained unless a considerable excess of the reagent is used. Hence, if the experiment be conducted under standardised conditions, it gives an approximate measurement also of the degree of mercerisation. Two solutions are required, viz. : (*a*) 1 grm. of iodine and 20 grms. of potassium iodide dissolved in 100 c.c. of water ; (*b*) 280 grms. of zinc chloride dissolved in 300 c.c. of water. Three mixtures of these solutions are prepared containing, respectively, 5, 10 and 20 drops of solution (*a*) in 100 c.c. of solution (*b*). Portions of the sample are immersed in these mixtures and the colour produced is observed. Hübner gives the following table of results :—

Strength of Caustic Soda Used to Mercerise.	5 drops (*a*) to 100 c.c. (*b*).	10 drops (*a*) to 100 c.c. (*b*).	20 drops (*a*) to 100 c.c. (*b*).
0° Tw.	Colourless.	Colourless.	Slightly red.
10° Tw.	Faint blue.	Faint brown.	Faint reddish-chocolate.
20° Tw.	,,	Chocolate-brown.	Bluish-chocolate.
30° Tw.	,,	Reddish-blue.	Dark reddish-navy blue.
40° Tw.	Very light blue.	Darker reddish-blue.	Black.
50° Tw.	Deeper blue.		
60° Tw.	Same as with 50° Tw.		
70° Tw.	Lighter than with 60° Tw.		

Sub-group (b).

Distinction between Flax and Hemp.—The distinction between flax and hemp is sometimes of importance. When the ultimate fibres are examined under the microscope it is found that whilst the flax fibres taper to a point, those of hemp have a blunt, rounded or knotty end ; also the cross-sections of flax

fibres are polygonal, those of hemp irregular. Hanauseck (*Z. Faber-Ind.*, 1908, 105) treats the fibres with a solution obtained by adding an excess of sulphuric acid to a solution of potassium bichromate. In a few seconds the fibres begin to swell and the liquor near to the fibres turns green. Air bubbles appear and assist in causing the active yellow liquor to displace the inactive green liquor around the fibres; this movement is further assisted by tilting the microscopic slide on which the fibres are resting. The linen fibres are found to swell more quickly than those of hemp. The surface of the fibre becomes irregular and dark patches are produced in both cases, but are more pronounced in the case of the hemp. The author, however, attaches most importance to the appearance of the linings of the canals of the treated fibres. The canal of the immersed linen fibre is somewhat similar to that produced when treated with cuprammonium solution; it is very narrow, wavy, irregular, and broken. The canal of the hemp fibre, on the other hand, is a straight, continuous, very plastic tube, which is in no case broken or undulating.

Haller (*Chem. Zentre,* 1920, II., 48) uses concentrated sodium hydroxide solution as a distinguishing reagent. The fibres of flax and hemp show quite different swelling phenomena on treatment with concentrated caustic soda. Flax swells uniformly, and the contents of the central canal show up distinctly, whilst the fibre substance becomes uniformly transparent. In the case of hemp the contours become irregular, the fibre remains non-transparent, and the wall of the central canal does not stand out distinctly. The diameter of the flax fibre increases on an average by about 83 per cent., that of the hemp fibre by only 25 per cent. The flax fibre in contact with the alkali makes lively worm-like contortions; the hemp fibre also bends about, but less vigorously. On treatment with cuprammonium reagent the flax does not show barrel-shaped swellings, but the hemp fibre does. If the fibres are dyed with a strong solution of Dianil Blue P.H. in concentrated caustic potash lye and examined under the microscope, the flax shows knotty swellings and cross lines at irregular intervals which are more deeply dyed; in the case of hemp there are numerous cross lines, but these are not appreciably darker in colour than the rest of the fibre.

A comparatively simple test is described by Nodder (*J. Soc. Dyers and Col.*, 1923, 122). Fibres carefully selected from all parts of the material are collected, cut into small pieces, and soaked in warm water. They are then teased out and held with fine-tipped forceps, working on a dark background, a watchmaker's eyeglass being useful. A single fibre is held over a small warm iron plate with the free end towards the experimenter. The fibres of flax and ramie always twist in a clockwise direction during drying, whereas hemp and jute always twist in the reverse direction. For most purposes it is sufficient to examine a hundred fibres in order to state the percentage of flax and hemp in a mixture, provided the sampling is properly carried out. It is to be noted that the first movement observed in bringing a wet fibre into a warm atmosphere is generally a slight twist in the "wet" direction, but the "drying" twist begins very quickly. The fibres twist as fast as they are removed with the forceps from the wet material if the atmosphere is warm and dry, and it is possible to examine six or more per minute.

Some of the multicellular vegetable fibres are distinguished by containing lignocellulose, and its identification will of course exclude those which do not contain it. Lignocellulose is present in hemp and jute. The aniline sulphate and phloroglucinol tests have been described already.

Distinction between Hemp and Jute.—Hemp and jute are very similar in properties, but jute gives a much stronger colour than hemp with aniline

sulphate and phloroglucinol. It has also a marked affinity for basic dyestuffs, whereas hemp has comparatively little.

Distinction between Cotton and Linen (W. Dickson, *Analyst*, 1925, 318).—When pure cotton is stained with silver nitrate, cleared with dilute nitric acid and examined under the microscope, it appears bright and shows all the characteristics of cotton fibres. Linen fibres, on the other hand, retain their dark stain even after clearing, and when examined under the microscope appear practically black and are invisible by polarised light. By turning the crossed Nicols attached to the sub-stage of the microscope, one can cut out the linen or cotton at will. Many other fibres such as hemp and Esparto stain like linen.

Group III.

Artificial Silks.

Nitro-cellulose and cellulose acetate silks are comparatively easy to identify, but artificial silks which consist of regenerated cellulose, such as cuprammonium silk and viscose silk, are very difficult to distinguish from one another.

Nitro-cellulose Silk.—Although nitro-cellulose silk is always denitrated, it still gives a strong reaction for nitro-groups. A fragment of diphenylamine is dissolved in concentrated sulphuric acid and the solution poured on to a little of the silk. If nitro-groups are present a deep blue colour is produced. It must be remembered that nitrates give the reaction also.

Cellulose Acetate Silk is soluble in acetone or chloroform. It is sometimes partly saponified to give it an affinity for direct dyestuffs. In this case only the unsaponified portion is soluble, but if a fabric containing cellulose acetate be warmed with acetone and the solvent poured off and allowed to evaporate, a film of cellulose acetate is obtained. Of the reactions which may be used for confirmatory tests the following are suitable :—

The Acetate Test.—A little of the silk is boiled with a solution of sodium hydroxide to saponify the cellulose acetate. The mixture is diluted with water and the regenerated cellulose filtered off. The filtrate is evaporated to a small volume and tested for acetates. If the solution be acidified with sulphuric acid and a little alcohol added, the smell of ethyl acetate is produced on warming. Or the solution may be made exactly neutral and a neutral solution of ferric chloride added ; if an acetate be present the liquid becomes red, and when boiled, insoluble basic ferric acetate is produced and acetic acid is evolved.

Clayton's Acetamide Test.—A hard glass tube is drawn off near the centre. A little ammonia solution is placed in it and some of the silk. The drawn-off portion of the tube is then sealed and the tube heated to about 140° C. in an oil bath for from 30 to 60 minutes. When cold the tube is opened and the smell of acetamide will be perceived.

Cellulose Silks.—If an artificial silk be neither nitro-silk nor acetate silk, it must consist of regenerated cellulose, for example, cuprammonium silk and viscose silk. The distinction between these depends chiefly upon the presence of unremoved impurities. Viscose generally contains traces of sulphur, cuprammonium silk does not. On the other hand traces of copper may be present in cuprammonium silk, although the absence of this metal must not be taken as proof that the sample is not of cuprammonium origin. Cellulose silks have most properties in common. They dissolve in concentrated sulphuric acid and are insoluble in 5 per cent. sodium hydroxide solution, Loewe's reagent and

Richardson's reagent. The action of concentrated sulphuric acid forms the basis of *Wilson's test*: When a small quantity (0·2 grm.) of the silk is treated with 10 c.c. of concentrated sulphuric acid in a test-tube, both the cuprammonium and viscose varieties dissolve. The former gives at once a yellow or brownish-yellow colour and the solution remains brownish-yellow after about 40 minutes. In the case of viscose the initial colour is reddish-brown, and after 40 minutes rusty brown.

Some of the other tests proposed are summarised in the table opposite. Some of the reagents used are:

(1) *Zinc Chloriodide.*—25 grms. of zinc chloride are dissolved in 12 c.c. of water and mixed with 1 grm. of iodine dissolved in 16 c.c. of water containing 5 grms. of potassium iodide. The mixture is allowed to stand for some time and the clear solution then decanted off.

(2) *Schweitzer's Reagent.*—Freshly precipitated cupric hydroxide is washed with distilled water until free from alkali and then dissolved in 20 per cent. aqueous ammonia. The solution is not very stable. It should be prepared frequently and kept in the dark.

(3) *Rhode's Solution.*—1 grm. of silver nitrate is dissolved in 10 c.c. of water and added to a solution of 4 grms. of sodium thiosulphate in 100 c.c. of water. After allowing the precipitate at first formed to dissolve, a solution of 4 grms. of sodium hydroxide in 100 c.c. of water is added and the mixture boiled and filtered. The silk is immersed in the solution for one minute at the boiling-point.

(4) *Sulphuric Acid and Iodine.*—1 grm. of potassium iodide is dissolved in 25 c.c. of water and crystals of iodine are added until the solution is saturated. The clear liquid is poured off and diluted to about three times its volume with water, and an equal volume of concentrated sulphuric acid is added slowly.

(5) *Ruthenium Red.*—$Ru_2(OH)_2Cl_4(NH_3)_7 . 3\,H_2O$, although expensive, is a useful reagent. According to Beltzer (*J. S. C. I.*, 1911, 1206) the reagent is made by dissolving 0·01 grm. of the salt in 10 c.c. of water. By its use viscose derived from wood pulp can be distinguished from that made from cotton. The solution does not stain normal cellulose but stains gums, pectins and oxycellulose. Lignified tissues are not stained ordinarily, but after treatment with alkali or sodium hypochlorite they are coloured bright pink. Viscose made from wood pulp gives a strong pink colour, whilst cotton and cuprammonium silk are barely stained. Before making a test all traces of acid must be removed by washing the sample in alkaline water.

According to Hoz (*Textilber*, 1929, **10,** 44) cuprammonium and viscose silks can be distinguished by the following reaction: The sample is treated in a test-tube for five minutes at atmospheric temperature with a solution of 15 c.c. of iron gall ink, 20 c.c. of a 0·5 per cent. solution of eosin and 30 c.c. of water, and then washed with water. Viscose gives a bluish-red colour, cuprammonium a pure blue. The eosin merely emphasises the reaction, it does not react alone. The iron gall ink consists of 25 grms. of Ether Tannin S, 7 grms. of Gallic Acid W. C. Cryst., 5 grms. of Ink Blue (all Geigy), 30 grms. of ferrous sulphate, 7 grms. of 20° Bé. hydrochloric acid, 1 grm. of phenol or salicylic acid, dissolved in one litre of water.

Casella's Test for distinguishing between viscose and cuprammonium silk may be mentioned. It consists of dyeing the samples with Naphthylamine Black 4B. Viscose is dyed a light reddish-grey and cuprammonium silk a dark bluish-grey. Krais (*Papier Fabr.*, 1926, **24,** 330) states that this and the Rhodes test are the most reliable.

The detection of cuprammonium silk is described also by Lang (*Textilber*,

<table>
<tr><th rowspan="2"></th><th rowspan="2">COTTON.</th><th rowspan="2">GROUP IIb.</th><th rowspan="2">SILK.</th><th rowspan="2">WOOL.</th><th colspan="4">ARTIFICIAL SILKS.</th></tr>
<tr><th>Acetate.</th><th>Nitro-</th><th>Cuprammonium.</th><th>Viscose.</th></tr>
<tr><td>Cold Conc. H_2SO_4</td><td>Soluble</td><td>Dissolve Slowly</td><td>Soluble</td><td>Dissolves Slowly</td><td colspan="4">Soluble</td></tr>
<tr><td>Cold Conc. HCl</td><td colspan="2"></td><td>Soluble</td><td>Insoluble</td><td colspan="4"></td></tr>
<tr><td>5 per cent. NaOH</td><td>Insoluble</td><td>Insoluble</td><td colspan="2">Soluble</td><td colspan="4"></td></tr>
<tr><td>Zinc Chlor-iodide</td><td>Blue</td><td colspan="7"></td></tr>
<tr><td>Schweitzer's Reagent</td><td>Dissolves Slowly</td><td></td><td>Fibroin Dissolves</td><td></td><td>Swells</td><td>Swells quickly and Dissolves</td><td colspan="2">Swell slowly and Dissolve</td></tr>
<tr><td>Dreaper's Reagent</td><td colspan="2">Not Coloured</td><td>Red</td><td>Dark Brown to Black</td><td colspan="4">Not Coloured</td></tr>
<tr><td>Millon's Reagent</td><td colspan="2"></td><td>Ordinary Red Tussur Brown</td><td></td><td colspan="4">Not Coloured</td></tr>
<tr><td>Wagner's Reagent</td><td colspan="2">Deep Brownish-red</td><td>Boiled-off Yellow Natural Brown</td><td>Deep Yellow</td><td>Intense Greenish-yellow</td><td>Not Coloured</td><td>Red</td><td>Not Coloured</td></tr>
<tr><td>Rhode's Solution</td><td colspan="4"></td><td colspan="3">No Change</td><td>Brown</td></tr>
<tr><td>Van Giesen's Solution*</td><td>Blue</td><td>Hemp—Violet-red Flax—Blue</td><td>Violet-red</td><td>Yellow</td><td colspan="4"></td></tr>
<tr><td>Ammoniacal NiO_2</td><td colspan="2"></td><td>Soluble</td><td></td><td colspan="4">Swell</td></tr>
<tr><td>Copper-Glycerol</td><td colspan="2"></td><td>Soluble</td><td></td><td colspan="4">No Change</td></tr>
<tr><td>$H_2SO_4—I_2$ Solution</td><td colspan="2"></td><td>Yellow</td><td></td><td>Yellow</td><td>Violet</td><td>Light Blue</td><td>Blue</td></tr>
<tr><td>Acetone</td><td colspan="2">Insoluble</td><td>Insoluble</td><td>Insoluble</td><td>Soluble</td><td colspan="3">Insoluble</td></tr>
<tr><td>Chloroform</td><td colspan="2">Insoluble</td><td>Insoluble</td><td>Insoluble</td><td>Soluble</td><td colspan="3">Insoluble</td></tr>
<tr><td>Acetic Acid</td><td colspan="2"></td><td>Dissolves on Boiling</td><td></td><td>Soluble</td><td colspan="3">Insoluble</td></tr>
<tr><td>Decolorised Magenta</td><td colspan="2"></td><td>Pink</td><td>Pink</td><td colspan="4">Not Coloured</td></tr>
<tr><td>Diphenylamine</td><td colspan="4"></td><td>Not Coloured</td><td>Deep Blue</td><td>Not Coloured</td><td>Not Coloured</td></tr>
<tr><td>Ruthenium Red</td><td colspan="2"></td><td>Rose</td><td></td><td>Not Coloured</td><td>Violet</td><td>Slight Pink</td><td>Pink</td></tr>
</table>

* See p. 14.

1923, 231, and *J. Soc. Dyers and Col.*, 1923, 225). The following solutions are required :—

Ferric chloride, ...	32·4 grms per litre.
Ammonium thiocyanate, . . .	76·1 ,,
Sodium thiosulphate, . . .	75 ,,

The sample to be tested is placed in a conical flask beside flasks containing samples known to be pure viscose and pure cuprammonium, respectively. Into each flask 15 c.c. of concentrated nitric acid are run and after standing for about a quarter of an hour the contents of the flasks are diluted to 200 c.c. with distilled water. 50 c.c. of each of the solutions are then transferred to large beakers and 25 c.c. of ferric chloride solution and 25 c.c. of thiocyanate solution added. The volumes are all made up to 400 c.c. with distilled water, and three test-tubes, each containing 15 c.c. of the thiosulphate solution, are emptied into the three beakers simultaneously. The presence of traces of copper causes the colour of the cuprammonium solution to fade much more quickly than in the case of the viscose, the one becoming colourless whilst the other is still deep red.

Some other sensitive tests for copper will be given in a later chapter.

Microscopic Examination.—When it has been determined that a sample is a regenerated cellulose artificial silk, microscopic appearance will assist in the distinction between viscose and cuprammonium origin in those cases, now rapidly becoming more common, where the yarn is of the fine filament type. Fine filament cuprammonium fibrils have a smooth surface and look just like real silk ; it is, in fact, often almost impossible to distinguish them from natural silk by their microscopic appearance. All viscose types, on the other hand, have well-marked longitudinal striations which easily distinguish them from the cuprammonium products. This test only applies in the case of the fine filament yarn, but since practically all cuprammonium silk is now of this type, the microscopic appearance is often of great assistance in arriving at a conclusion.

Certain viscose yarns, notably *Dulesco* and *Dulenza*, are made with a frosted surface, to give them a dull appearance more like real silk. These are recognised under the microscope by the pits on their surface. *Celta*, a hollow filament fibre, has a characteristic microscopic appearance which cannot be mistaken.

Structural Markings.—Most artificial silks show definite types of structural markings which can be classified as (1) well-defined striations, which follow the contour of the cross-sections, (2) fine striations, formed probably during the stretching of the fibre in the coagulating bath, (3) transverse striations or cracks, (4) round or elliptical markings like bubbles, (5) solid impurities, (6) faults such as swollen or contracted portions of the fibres. The main structures are usually strongly marked and seen best in oblique light or by dark-ground illumination. The bubble markings are also seen best by dark-ground illumination, and the fine longitudinal and transverse sections by transmitted light. Observations made with dark-ground illumination should be confirmed if possible by transmitted light, since the former tends to produce false images. For satisfactory dark-ground illumination with high objectives, a special dark-ground condenser must be used. (Lawrie, *J. Soc. Dyers and Col.*, 1928, 73.)

Interference Effects.—Artificial silks show strongly-marked interference colours when examined between crossed Nicol prisms. The fibres are mounted in euparal or Canada balsam. A Nicol prism is inserted in the sub-stage in place of the condenser and the analyser is screwed in behind the objective. A half-inch objective and a × 10 eye-piece give satisfactory results. The maximum colour is produced when the Nicols are crossed. When the polariser

is rotated through an angle of 45°, the colour is reduced to a minimum or zero, but when rotated through an angle of 90° a new range of colours is produced, these secondary colours being as a rule complementary to those produced by the crossed Nicols. The following are the typical interference colours described by Lawrie for the principal varieties of artificial silk :

Kind of Silk.	Principal Effects with Crossed Nicol Prisms.
Viscose, . . .	Yellow ground with red or orange-red central band. With polariser at 90° a blue fibre with a greenish-blue centre.
Cuprammonium, .	Yellow filaments changing to blue at 90°.
Cellulose nitrate, .	Very brilliant and diverse effects. Generally shows several bands of colour, *e.g.*, orange-red-yellow-green, changing at 90° to orange or greenish-blue.
Cellulose acetate, .	Uniform grey tint.
Sniafil, . . .	Plain yellow and at 90° plain blue.
Celta, . . .	Pale greenish or straw colour with crossed Nicols.

Ultraviolet Fluorescence.—Kopitsch (*Kunstseide*, 1928, **10**, 321) differentiates certain types of artificial silks by means of the fluorescence produced in ultraviolet light. Viscose shows a sulphur-yellow fluorescence characterised by bluish gradations, due to deflection of visible violet light passing through the filter of the ultraviolet lamp. Cuprammonium silk (Bemberg) shows a pink, cloudy fluorescence, with strong blue to bluish-violet gradations. Chardonnet silk gives a flesh-coloured fluorescence, and cellulose acetate a deep blue to violet fluorescence with strong bluish-violet gradations. Degummed silk shows a bright bluish fluorescence which is more intense than that of artificial silks.

The Swelling of Artificial Silks.—Lawrie (*loc. cit.*) found that the swelling power of artificial silks is a characteristic property. One filament is placed on a slide under a cover glass. About 20 measurements of diameter are then taken at different points along its length and the average found. A few drops of water are then run under the cover slip. The swelling is very rapid and in 10 minutes about 75 per cent. of the maximum has taken place. After an hour or two the final series of measurements is taken and the percentage increase in diameter estimated. To prevent evaporation the slides may be placed under a bell jar together with a dish of water. Another method is to suspend the fibre, weighted so that it hangs straight, in a small glass cell with water or other liquid, and examine it with the microscope, in a horizontal position.

Lawrie gives the following swelling powers for various artificial silks :

Type of Silk.	Increase in Diameter.
Viscose, ...	35 per cent.
Vistra, ...	52 ,,
Celta, ...	25 ,,
Tubize (Cellulose nitrate), .	30 ,,
Brysilka (Cuprammonium), .	53 ,,
Bemberg (Cuprammonium), .	41 ,,
Celanese, ...	9 ,,
Rhodiaseta (Acetate), . .	14 ,,
Courtauld (Acetate), . .	11 ,,
Lustron (Triacetate), . .	3 ,,

Artificial and Real Silks.—Artificial and real silks can be distinguished by diazotising and developing with β-naphthol. Formhals (*J. Soc. Dyers and Col.*, 1919, 222) gives the following test as suitable in the case of weighted silk: The sample is dissolved in concentrated sulphuric acid, the solution diluted and made alkaline with sodium hydroxide, and then treated with a solution of diazotised *p*-nitroaniline. Real silk gives a red colour and artificial silk a yellow colour.

The Identification of Fibres in a Mixture.

Microscopic examination of a mixture of fibres is assisted by applying some method of differential staining. Dyed fibres must of course be stripped first.

Dreaper's Reagent is made by adding 2 grms. of sodium hydroxide dissolved in 30 c.c. of water to 2 grms. of lead acetate dissolved in 50 c.c. of water. The mixture is boiled until it becomes clear, cooled to about 60° C., and 0·3 grm. of magenta dissolved in 5 c.c. of alcohol added. The solution is made up to 100 c.c. and filtered if necessary. A piece of the fabric to be tested is heated in this solution nearly to the boiling-point for 2 minutes, washed with water, then with dilute acetic acid, and dried. Silk will be coloured red and wool black, whilst vegetable fibres remain white. The magenta may be replaced by picric acid.

Van Giesen's Reagent consists of a solution of methylene blue and carbol-fuchsin. It gives the following colours:

Cotton, ramie, flax, cellulose silks, . .	Blue.
Wool, ...	Yellow.
Silk and hemp, ...	Violet-red.

Wagner's Reagent (Picrocarmine K.).—4 grms. of sodium ammonium phosphate and 1 grm. of sodium carbonate are dissolved in 25 c.c. of water. To this solution is added a mixture of 5 grms. of Picrocarmine (Merck) and 75 c.c. of water, and the whole is warmed until solution is effected. The material to be tested is steeped in the reagent for five minutes and washed with water. The following colours are given with different fibres:

Wool and boiled-off silk, . . .	Deep yellow.
Raw silk, ...	Deep brownish-red.
Natural vegetable fibres, . . .	Brownish-red to red.
Cuprammonium silk, . . .	Dark red when wet. Wine red when dry.
Viscose silk, ...	Unaltered.
Nitro-silk, ...	Unaltered.

The Determination of the Textile Fibres.

The quantitative determination of one fibre in the presence of another depends chiefly upon the following facts. Vegetable fibres are insoluble in boiling dilute sodium hydroxide solution, but animal fibres are soluble. Vegetable fibres dissolve readily in concentrated sulphuric acid. Silk is dissolved by cold concentrated hydrochloric acid, Loewe's reagent and Richardson's reagent.

Wool-Cotton Mixtures.—About 5 grms. of the sample are dried, weighed in a weighing bottle, and boiled for 10 minutes in a 5 per cent. solution of sodium hydroxide to dissolve the wool. The undissolved cotton is filtered off, washed with hot water, then with dilute acetic acid, and finally again with water, after which it is dried and weighed. From the weight of the dry cotton the percentage is calculated and the wool deduced by difference. In the case of unbleached cotton five per cent. of its weight should be added to the dried material.

Example.

	Weight of dry sample taken	4·900 grms.
	Weight of dry residual cotton	2·150 ,,
	5 per cent. of 2·150	0·107 ,,
∴	Weight of cotton (corrected)	= 2·257 ,,
	and percentage	= 46·06

For the determination of small amounts of wool in the presence of cotton Schultze (*Papier-Fabr.*, 1929, **27,** 299) recommends the following method: The sample is first extracted with alcohol, and then treated with excess of 80 per cent. sulphuric acid by shaking in a stoppered bottle. The cotton dissolves in about 5 minutes. The mixture is then poured into excess of cold water, the undissolved wool filtered off, washed with water, ammonia and again water, dried and weighed.

Wool-Silk Mixtures.—The weighed dry sample is soaked for 3 minutes in concentrated hydrochloric acid at a temperature of about 50° C. The undissolved wool is washed with hot water, dilute ammonia and again with hot water, after which it is dried and weighed.

Alternative method: The dried sample is warmed with Richardson's reagent for about 5 minutes to dissolve the silk. The residual wool is soaked for a few minutes in dilute hydrochloric acid to dissolve nickel, then washed as before, dried and weighed.

Silk-Cotton Mixtures.—The silk may be dissolved by treating the weighed sample for a few minutes with warm Loewe's solution. The undissolved cotton is rinsed with dilute hydrochloric acid, then washed with water until free from acid, dried and weighed. Richardson's reagent may be substituted for Loewe's reagent.

Silk-Wool-Cotton Mixtures.—The dry weighed sample is treated with Richardson's reagent to dissolve the silk. The residue is washed as described above, dried and weighed. The loss of weight gives the silk present. The residue is boiled with 5 per cent. sodium hydroxide solution to dissolve the wool and the residual cotton is washed, dried and weighed, the wool being obtained by difference. An alternative method would be to dissolve the silk with hydrochloric acid and then proceed as before.

Mixtures containing Artificial Silks.—It is very often necessary to analyse mixtures containing artificial silks, to determine the amount of duty which must be paid on them.

Acetate Silk with Wool or Natural Silk.—Acetate artificial silk differs from all the other textile fibres in its ready solubility in acetone. The sample to be analysed need only be dried, weighed and extracted with acetone in a Soxhlet extractor. The remaining silk or wool is then dried and weighed and the acetate silk obtained by difference, and, if it be desired, the solvent may be evaporated off and the cellulose acetate weighed as a check.

Acetate Silk and Cotton or Regenerated Cellulose Art Silks.—These mixtures

are analysed by the same method as that described in the preceding paragraph for animal fibres and acetate.

Animal Fibres, Cellulose Fibres and Acetate Silk.—In this case the acetate silk is dissolved out with acetone first and the residue weighed, the acetate being obtained by difference. The animal fibre is then dissolved with 5 per cent. boiling sodium hydroxide solution and the remaining cellulose fibre dried and weighed. This procedure is entirely suitable when dealing with cotton, but, for reasons to be explained later, it is not very accurate when dealing with regenerated cellulose artificial silks. When the latter are present more accurate results are obtained by extracting with acetone, then dissolving the viscose or cuprammonium yarn with Schweitzer's reagent, and finally weighing the remaining animal fibre. It must be remembered, however, that unbleached cotton loses 5 per cent. of its weight when boiled with alkali and this 5 per cent. must be added on to the weight of cotton found.

Mixtures of Silk or Wool with Regenerated Cellulose Art Silks.—For purposes where extreme accuracy is not essential, the method described for wool and cotton suffices. Viscose and cuprammonium silks, however, contain hemicelluloses, which are soluble in boiling caustic soda solution, and the method will, therefore, give low results for the artificial silk. More accurate results are given by the method described by Krais and Biltz (*J.S.C.I.*, 1920, 512 A), in which 0·2 to 0·5 grm. of the sample is treated twice for half an hour with 10 c.c. of cuprammonium solution. The residue is then washed once or twice with strong ammonia, once or twice in a 10 per cent. ammonia solution, then three times with water. This is followed by treatment with 10 per cent. hydrochloric acid, after which the residue is well washed with water, dried and weighed. The cuprammonium solution for this estimation is best prepared by passing air through a solution of ammonia (sp. gr. 0·925) in the presence of metallic copper for about three days. This method is not suitable for mixtures of real silk with cellulose artificial silks; the best method in this case is to estimate the nitrogen present by the Kjeldahl method (see page 61) and calculate the silk from the amount of nitrogen found. The nitrogen multiplied by 5·57 gives the weight of real silk. The silk cannot be extracted with Loewe's or Richardson's reagent in quantitative work because these solutions extract certain constituents from the artificial silk.

Cotton and Regenerated Artificial Silks.—There is no accurate method of separating these chemically. All that can be done is to weigh a portion of the fabric, unpick it and separate the yarns, and then weigh each constituent. In the case of fancy hose or half-hose, etc., the cotton or wool welt and the heel and sole (if composed of pure cotton) are carefully cut out and weighed, after the weight of the whole sample has been determined. If the remainder is then of homogeneous composition, only a portion of it need be unpicked, but, if this is not the case, the whole of it must be separated. Where the sample contains wool or real silk with cotton and regenerated cellulose silk, it is usual to dissolve the animal fibre in boiling 5 per cent. sodium hydroxide solution first, and then unpick the remainder.

The following chemical method has been proposed: Krais and Markert (*Rev. Gén. Mat. Col.*, 1931, **35**, 281) treat the material with a concentrated solution of calcium thiocyanate for one hour at 70° C., which dissolves viscose, cuprammonium silk, acetate silk, nitro-silk and natural silk, whilst raw and mercerised cotton and wool lose only from 2 to 4 per cent. by weight. Thorough stirring is necessary during the treatment, and the insoluble residue is collected by filtration through a metal sieve, washed with water, dried and weighed.

Lloyd and Priestley Method (*J. Soc. Dyers and Col.*, 1929, 201).—Regenerated cellulose silks are hydrolysed to soluble products by sulphuric acid of 69° Tw. (30 per cent. by volume) concentration, whilst cotton and wool are unaffected. The weighed sample is treated with 50 c.c. of the acid for 20 minutes, being pressed several times with a flattened glass rod. The liquor is decanted off, the remaining fibres pressed between the fingers, then washed successively with water, dilute ammonia, and water. The residue is dried and weighed. In a mixture of regenerated cellulose, cotton and wool, after removing the first, and weighing the cotton and wool, the cotton is dissolved by soaking in sulphuric acid of 69° Tw. for 24 hours at 25° C. Natural silk and regenerated cellulose may be separated by soaking 1 to 2 grms. of the sample for 15 minutes in 50 c.c. of hydrochloric acid of 21° Tw. at 50° C., the method being the same as that given above.

The United States Government gives the following general specification for testing textile materials :

" **Cotton.**—In specifications relating to cotton fibres no further test is needed in addition to the visual examination of the fibres as pulled from the specimen.

" **Wool.**—In specifications relating to all-wool fibres, chemical means shall be adopted to dissolve all the wool fibres, the impurities and vegetable fibres being left as indication of any variations from the all-wool requirements. Place the specimen of about 5 grms. in a beaker or vessel together with at least 100 times its weight of 5 per cent. solution of sodium or potassium hydroxide and boil slowly until the wool fibres become gelatinous and dissolve. If, after 10 minutes' boiling, there appear to be present any loose fibres or yarns on stirring with a glass rod, the contents shall be filtered through a fine mesh wire cloth and the residue washed with hot water. Allow the residue to dry in the air and then examine for its nature and determine the amount. If the presence of fibres and foreign matter is in excess of 1 per cent. in weight, it shall be cause for rejection.

" **Wool and Cotton Mixtures.**—In specifications relating to wool and cotton mixtures, chemical tests shall be made as follows : (*a*) With a cotton warp and no limit as to the amount of cotton allowed, based on the weight of the material as a whole, the filling shall be separated from the material until a weight of about 5 grms. is obtained. The test shall be made as for wool. (*b*) With a cotton warp and a limit as to the amount of cotton which shall be allowed, a specimen of about 5 grms. shall be weighed and placed in a beaker or vessel together with at least 100 times its weight of a 5 per cent. solution of sodium or potassium hydroxide and boiled slowly until the wool fibres become gelatinous and dissolve. After a period of 10 minutes' boiling, filter through a fine mesh wire cloth and wash the residue with warm water, then dry in the air and weigh. The percentage of cotton shall be calculated by adding 5 per cent. to the residual dry weight.

$$\frac{\text{Residue weight}}{100} \times 105 = \text{Weight of cotton.}$$

$$\frac{\text{Weight of cotton}}{\text{Original weight of specimen}} \times 100 = \text{Percentage of cotton.}$$

(*c*) With no mention as to where the cotton is to be found and with a limit as to the proportion of cotton allowed, the test shall be carried out as in (*b*).

" *Umpire Method for Wool and for Wool and Cotton Mixtures.*—In the event of a dispute, the following procedure shall be used : All weighings shall be

made after the specimen has been conditioned at 65 per cent. relative humidity and 70° F. Weighings shall be made to the nearest milligramme or equivalent accuracy. Boil at least 5 grms. of the specimen in at least 100 times its weight of a 5 per cent. solution of sodium or potassium hydroxide contained in an ordinary assay flask fitted with a reflux condenser for at least an hour. Pour the mass on a fine mesh wire cloth, wash first with warm water, then with a 3 per cent. solution of acetic acid and finally with hot water. The percentage of cotton shall be calculated by adding 5 per cent. to the residual dry weight, as expressed under (*b*) above." *Federal Specifications Board* (*U.S.A.*) *Specification No.* 345.

CHAPTER II.

PHYSICAL TESTS FOR TEXTILE MATERIALS.

Condition and Regain.

TEXTILE fibres are hygroscopic substances, which means that they can take up moisture from the atmosphere under suitable conditions. The process is reversible, however, and when exposed to an atmosphere with an excessively low relative humidity, the yarn will loose moisture and consequently weight. It follows, therefore, that the weight of a given sample of yarn or cloth may vary from day to day according to the atmospheric conditions, and if this is not borne in mind, considerable confusion may arise in all cases where transactions are carried out by weight.

Since a perfectly dry yarn does not exist under ordinary circumstances, it would not be convenient to base transactions on " dry weight." A certain standard " regain " has therefore been adopted for every type of fibre. This " regain " represents the proportion of water which perfectly dry yarn takes up when establishing equilibrium in an atmosphere of average humidity.

Textile materials are, by general consent, allowed to contain an amount of water equal to their " regain." When a sample contains exactly this amount it is said to be of " correct condition weight." In many transactions the goods are bought or sold on their " correct condition weight." This involves a moisture determination and a calculation of what the goods would weigh if they contained the standard amount of water. It follows that " conditioning," or the correction of weights for moisture, plays an important part in the textile trades, particularly in the case of the more expensive fibres such as silk.

Regains for Various Fibres.—It is most important to remember that the regain is not the actual percentage of water in the yarn at correct condition weight, but the amount taken up by 100 weight-units of the perfectly dry material. The regain of cotton is $8\frac{1}{2}$, but the percentage of water in it at correct condition weight is $\frac{100}{108 \cdot 5} \times 8 \cdot 5 = 7 \cdot 834$. The following are the standard regains for various yarns :

	Regain.	Percentage of Water Present when at Correct Condition Weight.
Cotton, ...	$8\frac{1}{2}$	7·83
Silk and artificial silk, .	11	9·91
Flax, ...	12	10·71
Hemp, ...	12	10·71
Jute, ...	$13\frac{3}{4}$	12·09
Carded woollen yarn, .	17	14·53
Worsted yarn, . . .	$18\frac{1}{4}$	15·43

The following are the regain standards of the Bradford Conditioning House for various types of wool:

Tops combed with oil,	19
Tops combed without oil,	$18\frac{1}{4}$
Noils, ordinary,	14
Noils, scoured or carbonised,	16
Worsted yarns,	$18\frac{1}{4}$
Cotton,	$8\frac{1}{2}$
Silk,	11
Wool and waste,	16
Worsted and woollen cloths,	16
Artificial silk,	11

It may be mentioned here that the figure of $18\frac{1}{4}$ is too high for wool and efforts have been made to have it lowered. Finished hosiery fabrics, for instance, rarely contain more than 12 to 13 per cent. of moisture, whilst a regain of $18\frac{1}{4}$ corresponds with 15·43 per cent. of water.

Determination of Moisture.—About one-half to one pound of yarn is necessary for each moisture determination. The sample is drawn from the bulk lot in such a way that it shall be truly representative. That is to say, hanks, cheeses or bobbins, whichever it may be, are drawn from different parts of the packing case containing the bulk sample. Where the material is not already in the form of hanks it must be wound off the tubes or bobbins on a wrap reel similar to that used in the determination of count.

When the hanks are ready, they are placed in a conditioning oven and carefully weighed. The conditioning oven (fig. 3) consists of a large air oven, heated electrically or otherwise. Attached to it is a relatively sensitive balance holding a weight pan at one end of the beam and a wire cage suspended in the oven at the other end. It is thus possible to weigh the sample without removing it from the oven and the danger that the extremely hygroscopic dry yarn may take up moisture from the atmosphere whilst being weighed is avoided. During the determination the temperature of the oven is maintained at 100 to 105° C., and the sample is allowed to remain in the hot chamber until no further loss of weight is observed.

Conditioning ovens may be heated by gas, electricity or steam, but unless a thermostat is provided the temperature must be watched carefully, because if it is allowed to rise too high, the material will be scorched and there will be excessive loss of weight owing to chemical decomposition of the fibre. According to Barker and Hedges (*J. Text. Inst.*, 1926, T 453) the material in the conditioning oven should be dried by a current of air which has been previously heated and dried, if the true moisture content is to be found. When the air has not previously been dried the results may be from 0·5 to 1 per cent. too low.

When large numbers of tests have to be made, the "Schopper" plant, provided with a pre-heating chamber, is to be recommended. The samples are all weighed and then put into a preparing oven through which the exhaust hot air from the real conditioning oven passes. In this way they are practically brought to a state of constant weight before entering the conditioning oven proper, where they are very rapidly brought to the dry state for the final weighing. Much time can be saved in this way since, as a rule, conditioning is a lengthy operation, owing to the long period during which the samples must remain in the oven to reach constant weight.

Calculation of Correct Condition Weight.—It is convenient to demonstrate the calculation of the correct condition weight with the aid of an example:

If two pounds of cotton yarn lose 4 ozs. in the conditioning oven, then 100 lbs. will lose 200 ozs. or 12·5 lbs. Therefore 100 lbs. of the sample contain 100 — 12·5 or 87·5 lbs. of dry yarn. Now we know that 100 lbs. of dry cotton are equivalent

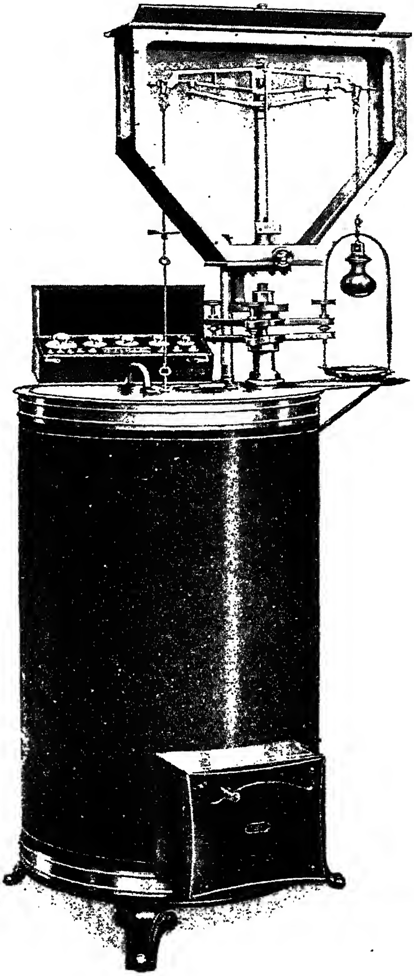


Fig. 3.—Electrically-heated "Conditioning Oven."—(*Goodbrand.*)

to $108\frac{1}{2}$ lbs. when at correct condition weight. Therefore 87·5 lbs. of dry yarn will be equivalent to $\frac{87 \cdot 5 \times 108\frac{1}{2}}{100}$ lbs. at correct condition weight, which is

94·94 lbs. The sample, therefore, contained 5·06 per cent. excess of water. Had the correct condition weight been 102·5, on the other hand, it would have shown that the sample contained less water than is allowed. We have, therefore, the following general equation for the calculation of correct condition weight:

$$\text{Correct condition weight} = \frac{y\,(100 + x)}{100},$$

where y = dry weight of 100 lbs. of sample to be tested,
x = regain of the fibre.

When a fabric contains more than one kind of fibre, the correct condition weight cannot be calculated until the proportion of each fibre present is known. This is first determined by chemical analysis, and the proportionate regain for each fibre is calculated, the final regain being the sum of these individual regains. Thus, if a fabric were found to contain 50 per cent. of wool and 50 per cent. of cotton, the regain would be

$$\frac{8{\cdot}5 \times 50}{100} + \frac{18{\cdot}25 \times 50}{100} = 13{\cdot}375.$$

Counts of Yarns.

The count of a yarn is a method of expressing its thickness or weight per unit length. Several systems of expressing counts are used for different fibres, as is shown in the list given below. A count is measured, as a rule, by the number of hanks required to weigh one pound. The hanks are standard lengths which differ for the different fibres or even for varying types of yarn spun from the same fibre.

Counts of Cotton Yarns.—*English System.*—The count is the number of hanks, each of which measures 840 yards, required to weigh 1 pound.

French System.—The number of 1,000-metre hanks which weigh 500 grms. gives the count. This in the English units of measurement is equivalent to the number of 992-yard hanks which weigh 1 lb.

Wool Counts.—*English Worsted.*—This count is given by the number of 560-yard hanks weighing 1 pound.

English Woollen.—The count is equivalent to the number of 256-yard hanks required to give 1 pound.

French Worsted.—Here the count is determined by the number of 1,000-metre hanks required to weigh 1,000 grms. It is equivalent to the number of 496-yard hanks to the pound.

Silk and Artificial Silks.—The counts are expressed in *deniers*. There are three different methods of measuring the count of a silk yarn:

The Italian Denier.—The weight of 450 metres expressed in deniers gives the count. The denier is an Italian weight standard which is equivalent to 0·05 grm. The following relationships assist in the conversion of Italian deniers into English metric system standards:

450 metres	=	492 yards.
33·33 deniers	=	1 dram (avoir.)
533·28 deniers	=	1 oz.
8532·48 deniers	=	1 lb.

The Metric Denier System.—The weight of 9,000 metres in grammes gives the denier of the yarn. Thus if 9,000 metres weigh 150 grms., the count will be 150 deniers. Actually these different systems do not give very different results, as shown by the following comparison:

System.	Comparative Weight of Standard Length of Yarn.
Italian, .	100
Metric, .	99·6

Spun Silk.—For spun silk the cotton system of expression is used.

The following table of equivalent counts is taken from the *Textile Recorder Year Book* :—

TABLE OF COUNT EQUIVALENTS.

Cotton Counts, 840 yds. Hank.	Equivalent Woollen Counts, 256 yds. Skein.	Equivalent Worsted Counts, 560 yds. Skein.	Equivalent Silk and Artificial Silk, Deniers.	Cotton Counts, 840 yds. Hank.	Equivalent Woollen Counts, 256 yds. Skein.	Equivalent Worsted Counts, 560 yds. Skein.	Equivalent Silk and Artificial Silk, Deniers.
1	3·28	1·5	5282·00	78	255·94	117·0	67·72
2	6·56	3·0	2641·00	80	262·50	120·0	66·03
3	9·84	4·5	1760·67	82	269·06	123·0	64·41
4	13·12	6·0	1320·50	84	275·62	126·0	62·88
5	16·41	7·5	1056·40	86	282·19	129·0	61·42
6	19·69	9·0	880·33	88	288·75	132·0	60·02
7	22·97	10·5	754·57	90	295·31	135·0	58·69
8	26·25	12·0	660·25	92	301·87	138·0	57·41
9	29·53	13·5	586·90	94	308·44	141·0	56·19
10	32·81	15·0	528·20	96	315·00	144·0	55·02
11	36·09	16·5	480·20	98	321·56	147·0	53·90
12	39·37	18·0	440·17	100	328·12	150·0	52·82
13	42·65	19·5	406·31	110	360·94	165·0	48·02
14	45·94	21·0	377·29	120	393·75	180·0	44·01
15	49·22	22·5	352·13	130	426·54	195·0	40·63
16	52·50	24·0	330·13	140	459·37	210·0	37·73
17	55·78	25·5	310·70	150	492·19	225·0	35·21
18	59·06	27·0	293·45	160	525·00	240·0	33·01
19	62·34	28·5	278·00	170	557·80	255·0	31·07
20	65·62	30·0	264·10	180	590·62	270·0	29·34
21	68·91	31·5	251·52	190	623·44	285·0	27·80
22	72·18	33·0	240·10	200	656·25	300·0	26·41
23	75·46	34·5	229·65	210	689·06	315·0	25·15
24	78·75	36·0	220·08	220	721·88	330·0	24·01
25	82·03	37·5	211·28	230	754·69	345·0	22·96
26	85·31	39·0	203·16	240	787·50	360·0	22·00
27	88·59	40·5	195·63	250	820·31	375·0	21·13
28	91·87	42·0	188·64	260	853·12	390·0	20·32
29	95·15	43·5	182·14	270	885·94	405·0	19·56
30	98·43	45·0	176·06	280	918·75	420·0	18·86
31	101·72	46·5	170·39	290	951·56	435·0	18·21
32	105·00	48·0	165·06	300	984·37	450·0	17·61
33	108·28	49·5	160·06	310	1017·19	465·0	17·04
34	111·56	51·0	155·35	320	1050·00	480·0	16·51
35	114·84	52·5	150·91	330	1082·81	495·0	16·01
36	118·12	54·0	146·72	340	1115·62	510·0	15·53
37	121·40	55·5	142·76	350	1148·44	525·0	15·09
38	124·68	57·0	139·00	360	1181·25	540·0	14·67
39	127·96	58·5	135·44	370	1214·06	555·0	14·28
40	131·25	60·0	132·05	380	1246·85	570·0	13·90
41	134·53	61·5	128·98	390	1279·66	585·0	13·54
42	137·81	63·0	125·76	400	1312·50	600·0	13·21
43	141·09	64·5	122·84	410	1345·31	615·0	12·90
44	144·37	66·0	120·05	420	1378·12	630·0	12·58
45	147·66	67·5	117·38	430	1410·94	645·0	12·28
46	150·94	69·0	114·83	440	1443·75	660·0	12·01
47	154·21	70·5	112·38	450	1476·56	675·0	11·74
48	157·50	72·0	110·04	460	1509·37	690·0	11·48
49	160·78	73·5	107·80	470	1542·19	705·0	11·24
50	164·06	75·0	105·64	480	1575·00	720·0	11·00
52	170·62	78·0	101·58	490	1607·81	735·0	10·78
54	177·19	81·0	97·81	500	1640·62	750·0	10·56
56	183·75	84·0	94·32	510	1673·44	765·0	10·36
58	190·31	87·0	91·07	520	1706·25	780·0	10·16
60	196·87	90·0	88·03	530	1739·06	795·0	9·97
62	203·45	93·0	85·20	540	1771·87	810·0	9·78
64	210·00	96·0	82·53	550	1804·69	825·0	9·60
66	216·56	99·0	80·03	560	1837·50	840·0	9·43
68	223·12	102·0	77·68	570	1870·31	855·0	9·27
70	229·68	105·0	75·46	580	1903·12	870·0	9·11
72	236·24	108·0	73·36	590	1935·94	885·0	8·95
74	242·80	111·0	71·38	600	1968·75	900·0	8·80
76	249·36	114·0	69·50	650	2132·81	975·0	8·13

Counts of Doubled Yarns.—In the case of two yarns being twisted together, a figure "2" is written separated from the figure expressing the count by a stroke. Thus, when we have two 20 wool yarns (worsted or woollen system) twisted together, the count is expressed as 2/20. The twenty it will be seen does not tell us the count of the composite yarn but only that of the two individual threads forming it. The count of the doubled yarn treated as if it were single would be 10. In the same way if we had a three-thread yarn composed of three strands of 36's, its count would be expressed 3/36.

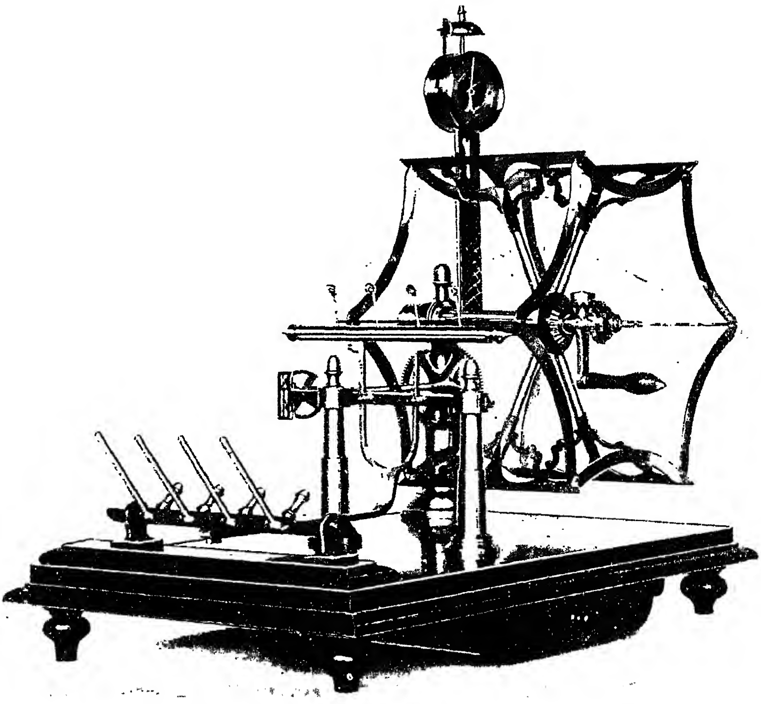


Fig. 4—Hand Wrap Reel.

The same principle is applied to cotton yarns. Here, however, the figure indicating the number of threads twisted together is frequently put after the count, thus 18/2. This is not a strict rule, but rather a matter of choice.

It is important to bear in mind that these remarks do not apply to spun silk. A 60/2 spun silk yarn means two 120 threads twisted together to give a composite yarn with a count of 60. In the case of silk or art silk expressed in deniers, a doubled yarn is expressed as in the case of cotton, that is to say, 150/2 means two 150-denier yarns doubled together.

Determination of Count.—In order to determine the count of a yarn, a suitable length is wound off on a wrap wheel (see fig. 4). One lea, consisting of 120

yards, is the length usually taken for the test. The length which has been wound off is recorded accurately on the dial attached to the wheel and it is generally arranged that a bell shall ring when one lea has been wound off.

Since the counts of yarns are rarely absolutely uniform it is necesssry to test several samples and calculate the mean count from the sum of all the results. It is as a rule necessary to carry out at least ten estimations to obtain a mean result which will be a reliable statement of the count.

The extent to which counts vary is shown in the following table (from *The Principles of Bleaching and Finishing of Cotton* (Trotman and Thorp) (Griffin)) :

Test No.	Weight of 120 Yards.	Count.
1	12·55 grms.	78·69
2	12·45 ,,	80·32
3	12·70 ,,	78·66
4	12·95 ,,	77·22
5	12·00 ,,	83·33
6	12·35 ,,	80·97
7	13·10 ,,	76·33
8	12·70 ,,	78·66
		Mean Count 79·27

It must not be considered that one lea should always be taken for the test. In the case of very fine yarns a greater length is necessary to minimise the effect of experimental error in weighing. Thus, the lengths required for testing cotton yarns are as follows :

Up to 40 count,	120 yards
40 to 80 count,	240 ,,
80 to 100 count,	480 ,,
Very fine count,	1,000 ,,

When greater lengths are wound off on a wrap wheel the total weight of the hank from which the sample is being wound must be noted before and after reeling, to ascertain if there has been any loss of moisture. Such loss is likely to occur where a large length of yarn is spread out as on a wrap reel in a dry atmosphere. Another precaution to take is to avoid overlapping, with resultant increasing of the diameter of the reel. This may be avoided by pushing the yarn which has been wound off to one side from time to time.

As soon as the leas are wound off they should be placed in stoppered bottles so that they shall not lose or gain moisture, and when all the ten or more are ready, they are weighed on a balance which is sensitive to at least one-tenth of a grain. The count can then be determined in the manner shown in the following example :—

The leas give an average weight per lea of 35 grains. 120 yards are 1/7 of a cotton hank (840 yards). Thus one hank will weigh 7×35 grains. There are 7,000 grains in a pound, therefore one pound of the yarn will contain $\frac{7000}{7 \times 35}$ hanks $= 28{\cdot}6$. The count of the yarn is therefore 28·6.

To give another example: Let us suppose that 120 yards of a woollen yarn weigh 55 grains. The hank is 256 yards in length. The count therefore will be $\frac{7000 \times 120}{256 \times 35} = 93{\cdot}74$.

Determination of the Denier of a Silk Yarn.—The following example will show how the denier (Italian system) of a silk yarn may be estimated :

492 yards weigh 5·55 drams. Now 492 yards are equivalent to one hank and 1 dram equals 33·33 deniers. Therefore 1 hank of the sample weighs $5{\cdot}55 \times 33{\cdot}33$ deniers $= 184{\cdot}98$ deniers. Thus the count is 184·98.

Moisture and Counts.—The methods described for the determination of counts are sufficiently accurate for most purposes, but when exceptional accuracy is necessary, as in the case of a dispute, the amount of moisture must be allowed for. In this case the lea is wound off and is then dried in a conditioning oven before it is weighed. To the dry weight the correct regain is added and the count is calculated from the correct condition weight of the yarn. The following is a numerical example of the manner in which the calculation is carried out: If the dry weight of one lea of cotton is 40 grains, then the correct condition weight will be $\frac{40 \times 108{\cdot}5}{100}$ grains, which is 43·4 grains. The count of the yarn is therefore $\frac{7000}{7 \times 43{\cdot}4} = 23{\cdot}0$.

Oil in Yarns.—Another source of error in the determination of counts is that the sample of yarn may contain a considerable percentage of oil, all of which is weighed as yarn proper. Where an accurate determination is necessary, the oil must first be extracted and the yarn then dried before it is weighed. The allowance for condition is added and the count is calculated from the corrected figure for weight. Alternatively the percentage of oil present may be determined and deducted from the weight of the lea of yarn in the dirty state.

Count-testing Balances.—There are many special types of balances which give counts directly. Among these are the "Quadrant" balance and the "Knowles" balance.

The Determination of Tensile Strengths of Textile Materials.

The examination of the strengths of textile materials falls under three headings, namely :

(1) The testing of individual fibres.
(2) The testing of yarns.
(3) The testing of fabrics.

The Determination of the Tensile Strengths of Individual Fibres.—One of the simplest methods of examining the fibres for strength is that of O'Neill (*J. Text. Inst.*, 1924, T 282). The apparatus used is shown in fig. 5. The cylinder A is about 50 cm. long and about 6 cm. wide. The fibre is mounted with sealing wax across a hole 1 cm. wide in a sheet of paper, P. The ends of the paper are fixed in the positions K_1 and K_2 in the apparatus and the sheet is cut along the dotted lines. Water is now allowed to run out of the cylinder A until the fibre just begins to bear the weight of the float, when the tap is turned off. A graduated cylinder is then placed beneath the outlet and water is allowed to flow out through the tap until the fibre breaks, when the volume in the measuring cylinder is noted. The breaking strain in grammes is given by

$$\frac{Vr^2}{R^2 r^2}$$

where $V =$ the volume of water run out in cubic centimetres,
$R =$ the radius of the cylinder in centimetres,
and $r =$ the radius of the float in centimetres.

A very useful apparatus is described by Krais (*J. Text. Inst.*, 1928, T 32). It is manufactured by Messrs. Keyl of Dresden, under the name of " Deforden."

Determining the Tensile Strengths of Yarns.—There are two methods of estimating the tensile strengths of yarns, namely, the hank test and the single thread test.

The Hank Test.—The machine used to find the breaking strain of hanks is shown in fig. 6. The hank is stretched over the two hooks as shown in the figure. Tensional strain is sometimes applied by turning a handle, causing a weighted pendulum, which is attached to the top hook by a chain which passes over a pulley, to be pulled outwards through an angle which is proportional to the stress. The axle of the pulley over which the chain runs is attached to the pointer on the dial, and by this means the weight applied to the hank is

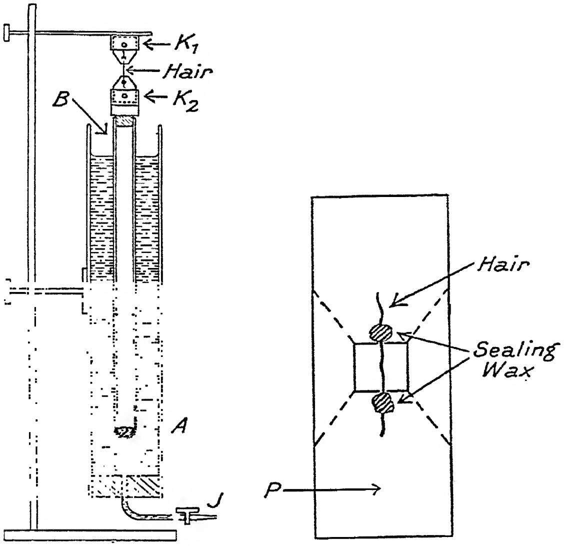


Fig. 5.—O'Neill's Breaking-load Tester.

registered. By a ratchet arrangement the pendulum remains stationary until it is released after the hank has broken. The strength is determined by the readings on the scales adjacent to the hooks holding the yarn. The actual extension will be the reading of the bottom hook less that of the top hook. This subtraction is necessary to allow for the movement of the top hook during the test. Before the test is commenced just enough tension must be applied to straighten the yarn ; the positions of the hooks on the extension scales must then be noted, and if they are not zero in each case, due allowance must be made. In using a hand-operated machine it is most important to turn the handle steadily and avoid all jerks, since the latter will put undue strain on the yarn. Further, if several hank tests are being made, an endeavour should be made to turn the handle at the same speed throughout the whole series of tests, since the results will be affected, to some extent, by the rate at

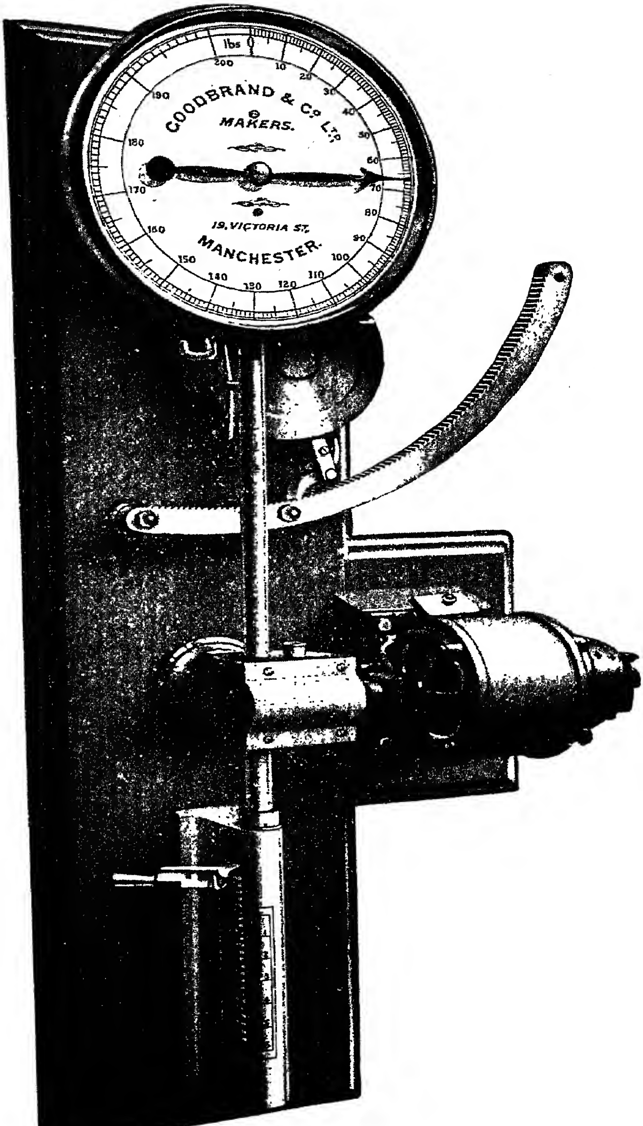


Fig. 6.—Yarn-testing Machine.

which the tension is applied. It is extremely difficult to maintain a steady, uniform rate of turning by hand, and for this reason the best testing machines are driven by an electric motor (see fig. 6).

The result of the hank test is usually expressed in pounds per lea; in other words the number of pounds necessary to break one lea of 120 yards. When the leas are wound on a wrap wheel of standard diameter there will always be the same number of threads to take the weight.

The disadvantage of the hank test is that it does not sufficiently emphasise the weak spots in the sample, since the adjacent threads are assisting in bearing the strain, and it is the weak parts of the yarn which break up in practice and cause trouble. Another drawback is that the results are influenced by the manner in which the lea is spread out on the hooks, and it is difficult to be certain that the leas will always be arranged in exactly the same way in two or more successive tests.

Hall (*J. Text. Inst.*, 1925, T 223) finds that for wool yarns the hank test will grade a series of samples in approximately the same quantitative order as single-thread tests. Since comparative results are generally required rather than absolute ones, it follows that the hank test is satisfactory. For good results, however, the testing machine must be power-driven and the rate of descent of the lower hook should be 12 inches per minute.

There are so many factors in yarn testing liable to produce false results, that an average figure should always be worked out from a number of tests.

Single Thread Tests.—Much more reliable results are obtained by testing the tensile strengths of single threads of the yarn. Here again it is most important that the weight should be applied uniformly if concordant results are to be obtained. The simplest single thread testing machines are operated by a handle, but it is almost impossible to obtain the desired regularity in application of the load in this way. The best machines are now made so that the weight can be applied by a plunger working in a cylinder of oil; in this way very uniform stretching is achieved. Alternatively, hydraulic arrangements may be used, or an air piston.

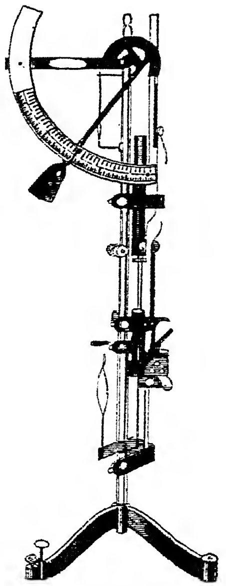


Fig 7.—Baer Single Thread Testing Machine.

A typical single thread testing machine working on the oil-plunge system is shown in fig. 7. The pendulum and pointer are similar to those described in the case of the hank-testing apparatus. The stretch of the yarn is automatically shown on a scale. Before use the instrument should be levelled. A small plummet is provided to facilitate this. The oil cylinder is filled with a good machine oil and the plunger made to ascend and descend several times in order to expel all the air bubbles. The rate of descent must be adjusted to 1 inch in five seconds by means of the nuts which are situated at the top of the cylinder. When the plunger has been pulled to the top of the stroke, it is held in position by a catch and cannot descend again until a trigger is released. The machine has a range of from 0 to 6 lbs. when the weight is attached to the pointer arm and a range up to 1 lb. when this weight is removed. The weight should

always be removed when the yarn is sufficiently fine to break with a load of less than 1 lb., as the readings will be more sensitive.

It is also possible to attach an arrangement to a testing machine by the aid of which the extension and the breaking strain are automatically recorded on a chart. The curve obtained has the form shown in fig. 8. The distance *b* is proportional to the breaking load and *a* represents the extension.

The results of tensile strength tests, even on the same yarn, always show considerable variation. Therefore a result has no value unless it is the mean of several readings. At least twenty readings should be observed, and even more than this may profitably be made if an exceptionally reliable result is required.

An automatic machine which will test several single threads at a time and record their breaking loads on a chart, is made by Messrs. Cook of Manchester, (see fig. 9). The following description is taken from the *Textile Recorder Year Book*, 1924: "The cops or bobbins holding the yarn are placed on skewers mounted upon a frame having a traversing motion. Each thread is passed through the tensioning hooks and eyes and between clips. When the machine is started the frame moves forward and a plate lying underneath the threads rises and places each thread into the jaws of another series of clips which immediately close. When the frame or carriage has receded about twelve inches, the clips on the carriage close on the threads, and as the carriage continues its forward movement for about another four inches, strain is put on the threads. The strain distends a series of springs mounted at the rear end of the second set of clips. The distension draws a series of pointers along until the several threads are broken; then the pointers are pressed down into the diagram slip, at the positions to which they have been pulled, and thus a record of the breaking load is made. The broken ends are cleared away from the clips, the pointers pushed back to zero, and the whole cycle of movements is repeated about eighty times, when the machine is stopped automatically. The record of the breaking strains of the threads is shown on a punctuated slip and variations are very readily observed. Different sets of springs are used for different qualities and counts of yarns.

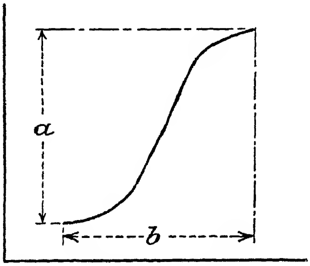


Fig. 8.—Breaking Load-Extension Curve.

"The only apparent weak point of the machine is the springs, and to eliminate error the greatest possible care is taken in their selection."

Effect of Moisture on Tensile Strength.—Shorter (*J. Soc. Dyers and Col.*, 1924, 300) finds that the presence of moisture causes a decrease in the tensile strength of wool fibres. Hardy (*J. Agric. Res.*, 1918, **14**, 285) also found that an increase in the humidity was accompanied by a decrease in the tensile strength. On the other hand the elasticity was found to be directly proportional to the amount of moisture present; this is illustrated by the following figures:

Humidity.	Elasticity.
27·8	40
39·08	80

The same author (*J. Agric. Res.*, 1920, **19**, 55) later showed that the tensile strength decreased up to 80 per cent. relative humidity, but after that increased as the amount of water vapour present became greater. From these facts it

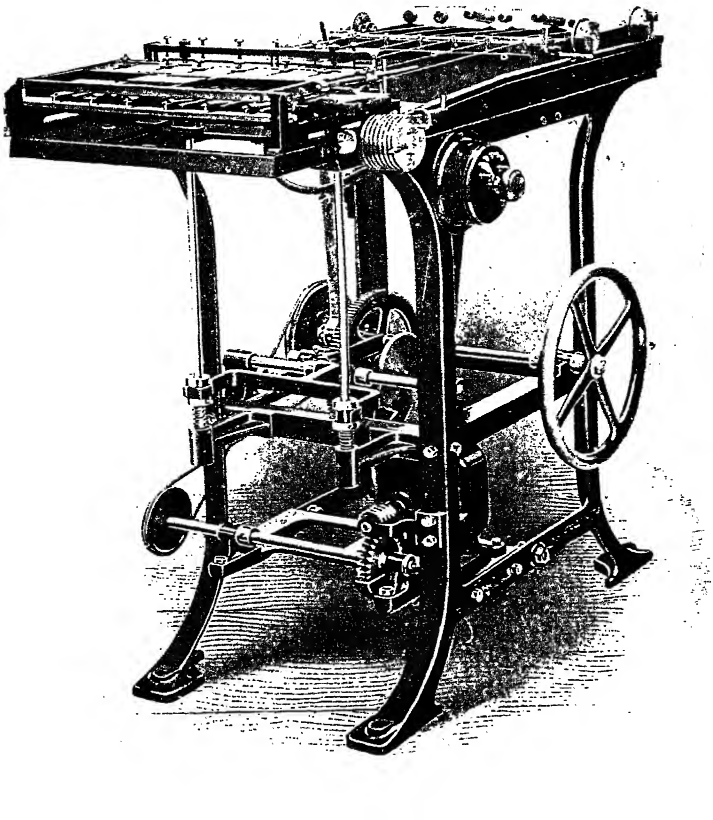


Fig. 9.—Cook's Single-thread Testing Machine.

will be apparent that precautions must be taken to ensure a constant humidity if accurate tensile strength results are desired.

In the case of cotton and flax, humidity has the opposite effect upon tensile strength, this and elasticity both increasing as the moisture content increases.

Artificial silk and true silk behave like wool. The following figures refer to a two-fold Egyptian cotton yarn of 100/2 count:

Humidity.	Tensile Strength.
37 per cent.	67·0
79 „	69·5
87 „	70·3

The Relation between the Hank Test and the Single Thread Test.—From the results of a large number of tests it has been found that the relation between the lea test and the single thread test is as 100 is to 0·88 (*Textile Recorder Year Book*, 1931, 381). Thus a yarn having a mean single thread breaking strain of 8·25 ozs. will give a lea test of 58·8 lbs., as shown by the following expression

$$(0{\cdot}88 \times 16) : 100 :: 8{\cdot}25 : x,$$

where x is the required lea strength.

The Breaking Length of Threads.—This is the length of a yarn which is necessary to break the yarn under its own weight when it is suspended. It gives a figure by the aid of which it is possible to compare the tensile strengths of yarns of different counts. The breaking length in the case of cotton is:

$$\frac{\text{Tensile strength of single thread in ozs.,} \times \text{count} \times 840}{16}.$$

For worsted yarns 560 must be substituted for the figure 840 in the numerator and in the case of woollen yarns 256 is substituted.

With ordinary pendulum testing machines there is a tendency towards a jerky movement of the pendulum as the load is applied. It has been stated that this is due to irregular slipping of fibre over fibre. Shorter and Hall, however, have shown that it is due entirely to the inertia of the moving parts of the apparatus (*J. Text. Inst.*, 1923, T 501).

A yarn testing machine described by Shorter and Hall (*J. Text. Inst.*, 1923, T 493) allows the elasticity of yarns or fibres to be studied with great accuracy.

Testing Fabrics.—It is frequently necessary to test the tensile strength and elasticity of fabrics. The machines used for this purpose are similar in principle to those used for yarn testing. An illustration of a typical hand-driven cloth testing machine is shown in fig. 10. The sample is clamped between the jaws, each of which is 4 inches wide. The distance between the jaws is 12 inches. The wheel is rotated, causing the lower jaw to descend. The breaking load is recorded on the dial and the stretch is shown on the scale. This apparatus can be driven mechanically if desired. It is of the utmost importance that the tension shall be applied evenly, and for this reason those machines which are operated by electric motors are to be preferred.

Determination of the Twist of Yarns.—There are two types of twist in a yarn which may have to be examined. In the first place there is the twist applied to the yarn when it is spun from the fibres, and secondly the twisting of two yarns together to give a doubled yarn. In each case the same type of instrument is used, a greater length of yarn being required for the determination of the twist in a doubled yarn than is necessary to test the twist applied during spinning.

The simplest type of apparatus is shown in fig 11, on which lengths of from one inch to twelve inches may be examined. The carriage bearing the dial and wheel is set so that a suitable length of yarn is taken. The dial is fixed by a locking screw and when this is loosened the reading may be set to zero before commencing the test. The sample is fixed in the two jaws and is unwound until there is no twist left. If there is any difficulty in determining this point it will be noticed that when it has been just passed the yarn commences to become twisted again. The end point can also be found by running a needle up the yarn, for there will be no resistance when fully untwisted. The number of revolutions which have been made is indicated on the dial, and by dividing this by the number of inches tested, the twist per inch can be found. Several readings should be taken and the variation noted, since it is usually more important to ascertain if the sample is uniform than the actual value of the twist. When dealing with a single yarn it is generally sufficient to take one inch, but to find the twist put into the doubling of two yarns ten to twelve inches must be taken.

Fig. 12 shows a more delicate instrument. It is supplied with a mechanism which ensures that there shall be the same amount of stretch on the yarn in every test. The magnifying glass which is supplied considerably facilitates the observation of the point at which the yarn becomes fully untwisted. Further, the take-up in length during spinning or doubling is recorded.

The twist is a very important factor which influences the tensile strength. Lack of twist is accompanied by weakness, and hence a sample which has irregular twist will also have weak spots which will cause trouble in weaving or knitting.

Examination of Yarns for Regularity.—The simplest method of examining the regularity of a yarn is to wind it off on an "examining board" in such a way that the threads do not overlap one another and view through a magnifying lens. More delicate apparatus has been described by Oxley (*J. Soc. Dyers and Col.*, 1923, 175).

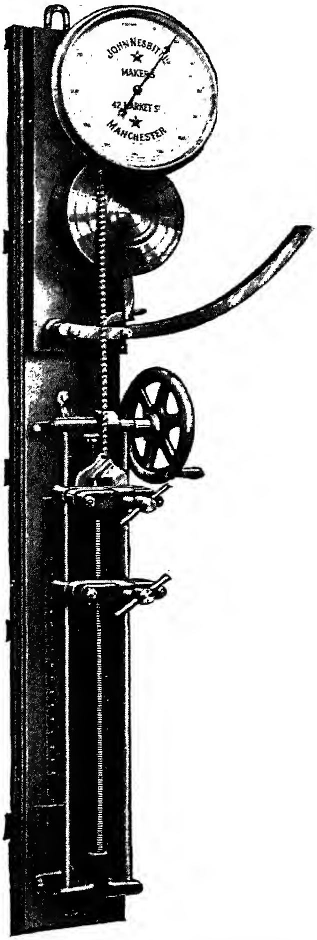


Fig. 10.—Cloth Testing Machine.

Determination of the Diameter of Fibres.—Three methods are available for the determination of the diameter of a fibre, viz., (1) measurement with calipers, (2) microscopic measurement, (3) measurement by means of a microbalance. The first of these methods is the simplest and calipers capable of measuring 0·01 mm. can be obtained.

For the measurement of diameters by means of a microscope, either a stage micrometer or a micrometer eyepiece is required. The former as made by Beck consists of a glass slip, 3 inches long and 1 inch wide, ruled with lines 0·1 mm. and 0·01 mm. apart. If this slip be placed on the stage of the microscope

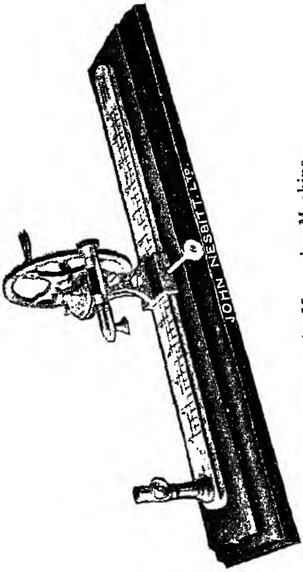


Fig. 11.—Twist Measuring Machine.

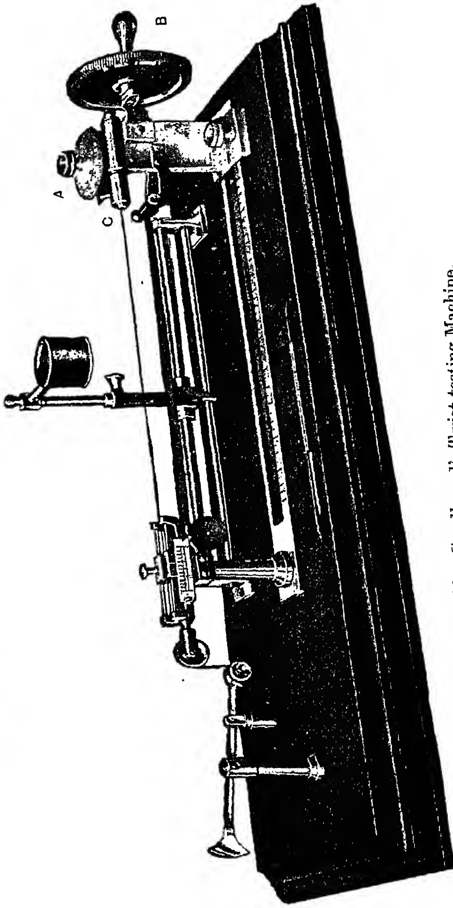


Fig. 12.—Goodbrand's Twist-testing Machine.

and viewed under the same conditions as the object, the space occupied by the diameter of the fibre can be read off directly. A micrometer eyepiece consists of a plate of glass ruled with very fine lines a definite distance apart, which can be put into the eyepiece of the microscope, the diameter of the fibre being measured directly.

The determination of diameter by means of a balance consists of finding the weight of a number of known lengths. Roberts (*J. Text. Inst.*, 1927, T 48)

recommends the use of a torsion balance, whilst Nernst's microbalance may also be used.

Barker and King (*J. Text. Inst.*, 1926, T 68) use the following formula for calculating diameter in the case of wool fibres, assuming that these possess a cylindrical structure :

$$W = \cdot \Delta\, d^2 l \quad \text{or } d^2 = \frac{4\,W}{\pi \Delta l},$$

where l = length of fibre, Δ = density, d = diameter, $\pi = \frac{22}{7}$ and W = weight of dry fibre as determined by the microbalance.

If conditioned instead of dry fibres are used, then $\frac{100\,W_r}{100+R}$ is the dry weight, where R is the regain and W_r the conditioned weight. Therefore for dry fibres

$$d^2 = \frac{400\,W_r}{\pi \Delta l\,(100 + R)}.$$

According to Calvert and Harland (*J. Text. Inst.*, 1924, T 8) and Clegg and Harland (*J. Soc. Dyers and Col.*, 1924, 55), the diameter of fibres may be measured by mounting transverse sections on a microscopic slide and drawing the image projected by a camera lucida on a sheet of paper of standard thickness. The tracings are cut out and weighed, their weights being proportional to the area of cross-section of the fibres.

Wear-testing Machines.—An apparatus for testing the wearing properties of yarns has been described by New (*J. Text. Inst.*, 1927, T 595) and one for fabrics by Morton and Turner (*J. Text. Inst.*, 1928, T 201). In the latter the cloth is clamped over a plate of mild steel, and a carborundum roller is caused to travel backwards and forwards over it for a definite time. The breaking strength of the cloth is tested before and after this treatment, the diminution being a measure of the damage caused by the treatment.

CHAPTER III.

DETERMINATION OF SPECIFIC GRAVITY AND VISCOSITY.

Specific Gravity.

It is a common practice in textile and other industries to check the strength of solutions of chemicals by means of specific gravity. Hydrometers are always used for this purpose. The result obtained is not strictly accurate and of course altogether unreliable unless the hydrometer is used at the temperature of calibration. Hydrometers are of two kinds, namely, those which give specific gravities directly and those which are graduated upon some arbitrary scale.

The Twaddell hydrometer is an example of the arbitrary instrument, the graduations being placed at such distances apart as to represent equal differences in specific gravity. The relation between degrees Twaddell and specific gravity is given by the formula

$$°\text{Tw.} \times 0{\cdot}005 + 1 = \text{specific gravity.}$$

In the case of the Baumé hydrometer the formula for liquids heavier than water is

$$\frac{145}{145 - °\text{Bé.}} = \text{specific gravity.}$$

The table opposite gives the equivalent values of specific gravity in terms of degrees Twaddell and degrees Baumé.

Specific gravity balances give more accurate results than hydrometers and are more suitable than the latter for laboratory use.

The Specific Gravity Balance.—Specific gravity balances are generally instruments of the steelyard type constructed to show the specific gravity of a liquid by the loss in weight of a plummet of known displacement when suspended in the liquid. The complete instrument, fig. 13, comprises the balance proper, a glass thermometer, the plummet and two exactly similar sets of rider weights of which the largest is equal to the weight of water displaced by the plummet at 15·5° C.

The plummet is generally designed to displace exactly 10 grammes of water at 15·5° C. The weight of the largest rider is therefore 10 grms., the next 1·0 grm., followed by riders weighing 0·10 and 0·010 grm. The beam of the balance is divided by notches into 10 equal parts which are numbered consecutively from 1 to 9. After the instrument has been mounted, the glass plummet is suspended from the knife edge of the divided beam and the beam brought to equilibrium (zero reading on the scale) by adjusting the counterpoise. If the plummet is then suspended in water at a temperature of 15·5° C., equilibrium should be restored by placing the large rider (10 grms. weight) on the hook from which the plummet is suspended. If the beam is not brought into equilibrium in this way the instrument is probably designed for use at some other temperature and a fresh set of weights will require to be made for use with the instrument.

Comparison of Hydrometer Degrees according to Baumé and Twaddell with the Specific Gravities.

Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.
0	0	1·000	19·3	31	1·155	36·0	66·4	1·332
0·7	1	1·005	19·8	32	1·160	36·2	67	1·335
1·0	1·4	1·007	20·0	32·4	1·162	36·6	68	1·340
1·4	2	1·010	20·3	33	1·165	37·0	69	1·345
2·0	2·8	1·014	20·9	34	1·170	37·4	70	1·350
2·1	3	1·015	21·0	34·2	1·171	37·8	71	1·355
2·7	4	1·020	21·4	35	1·175	38·0	71·4	1·357
3·0	4·4	1·022	22·0	36	1·180	38·2	72	1·360
3·4	5	1·025	22·5	37	1·185	38·6	73	1·365
4·0	5·8	1·029	23·0	38	1·190	39·0	74	1·370
4·1	6	1·030	23·5	39	1·195	39·4	75	1·375
4·7	7	1·035	24·0	40	1·200	39·8	76	1·380
5·0	7·4	1·037	24·5	41	1·205	40·0	76·6	1·383
5·4	8	1·040	25·0	42	1·210	40·1	77	1·385
6·0	9	1·045	25·5	43	1·215	40·5	78	1·390
6·7	10	1·050	26·0	44	1·220	40·8	79	1·395
7·0	10·2	1·051	26·4	45	1·225	41·0	79·4	1·397
7·4	11	1·055	26·9	46	1·230	41·2	80	1·400
8·0	12	1·060	27·0	46·2	1·231	41·6	81	1·405
8·7	13	1·065	27·4	47	1·235	42·0	82	1·410
9·0	13·4	1·067	27·9	48	1·240	42·3	83	1·415
9·4	14	1·070	28·0	48·2	1·241	42·7	84	1·420
10·0	15	1·075	28·4	49	1·245	43·0	84·8	1·424
10·6	16	1·080	28·8	50	1·250	43·1	85	1·425
11·0	16·6	1·083	29·0	50·4	1·252	43·4	86	1·430
11·2	17	1·085	29·3	51	1·255	43·8	87	1·435
11·9	18	1·090	29·7	52	1·260	44·0	87·6	1·438
12·0	18·2	1·091	30·0	52·6	1·263	44·1	88	1·440
12·4	19	1·095	30·2	53	1·265	44·4	89	1·445
13·0	20	1·100	30·6	54	1·270	44·8	90	1·450
13·6	21	1·105	31·0	54·8	1·274	45·0	90·6	1·453
14·0	21·6	1·108	31·1	55	1·275	45·1	91	1·455
14·2	22	1·110	31·5	56	1·280	45·4	92	1·460
14·9	23	1·115	32·0	57	1·285	45·8	93	1·465
15·0	23·2	1·116	32·4	58	1·290	46·0	93·6	1·468
15·4	24	1·120	32·8	59	1·295	46·1	94	1·470
16·0	25	1·125	33·0	59·4	1·297	46·4	95	1·475
16·5	26	1·130	33·3	60	1·300	46·8	96	1·480
17·0	26·8	1·134	33·7	61	1·305	47·0	96·6	1·483
17·1	27	1·135	34·0	61·6	1·308	47·1	97	1·485
17·7	28	1·140	34·2	62	1·310	47·4	98	1·490
18·0	28·4	1·142	34·6	63	1·315	47·8	99	1·495
18·3	29	1·145	35·0	64	1·320	48·0	99·6	1·498
18·8	30	1·150	35·4	65	1·325	48·1	100	1·500
19·0	30·4	1·152	35·8	66	1·330	48·4	101	1·505

To determine the specific gravity of a liquid, the plummet is immersed in the liquid contained in the immersion vessel and brought to the required temperature. If the liquid is lighter than water the large rider must be placed somewhere on the divided beam to produce equilibrium. If this occurs at some point intermediate between two notches the rider is placed in the notch of lower value of the two and the next rider is applied to determine the difference. Should the position of this rider also fall between two notches it is placed in the notch of lower value and the third rider brought into use, and so on. If the liquid is heavier than water, *i.e.* if it has a specific gravity greater than one, the same procedure is adopted, except in so far that the large rider is always hung from the hook on which the plummet is suspended.

For example, suppose in the case of a liquid lighter than water the large

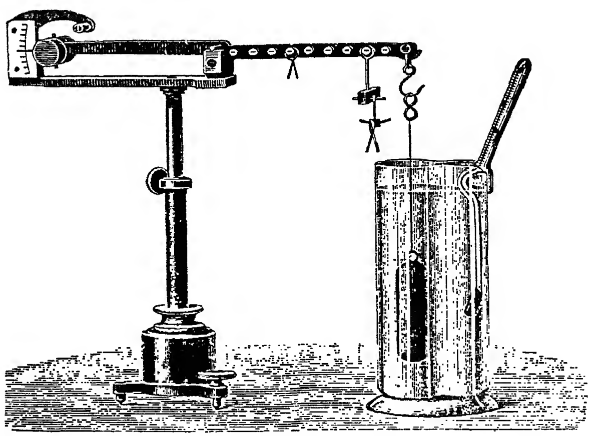


Fig. 13.—Specific Gravity Balance.

rider is in the eighth notch, the second rider in the ninth notch and the third and fourth riders both in the fifth notch ; the sp. gr. of the liquid will be

$$0{\cdot}8 \times 1 + 0{\cdot}9 \times 0{\cdot}1 + 0{\cdot}5 \times 0{\cdot}01 + 0{\cdot}5 \times 0{\cdot}001 = 0{\cdot}8955.$$

Specific Gravity Bottles.—When an accurate determination of specific gravity is required, either a specific gravity bottle or a Sprengel tube is always employed. Specific gravity bottles are of two kinds, illustrated by figs. 14 and 15, invented by Gay Lussac and Regnault, respectively. In the first type (fig. 14) the stopper is perforated by a capillary, which is filled with liquid when the stopper is inserted. In the Regnault type (fig. 15) the bottle is filled up to a mark on the constricted neck by means of a glass tube drawn out to a fine capillary at one end. The type of bottle used depends upon the nature of the liquid under test, the Regnault bottle being more suitable for those liquids which are either volatile or viscous.

A Sprengel tube, or pyknometer, fig. 16, has the advantage that its capacity need not be so great as that of a specific gravity bottle, and hence it can be used when only a small quantity of a liquid, *e.g.* 5 c.c., is available. The ends of

the capillaries are fitted with ground-on caps and on one of the capillaries a mark is etched between the cap and the U-tube. The cleaning of the pyknometer is carried out as described for the bottle form of apparatus. The instrument is filled by dipping the marked capillary in the liquid and applying suction at the other capillary until full. The instrument is then placed, with the caps on, in a thermostat for 15-30 minutes and the volume adjusted to the mark by withdrawing liquid from the plain capillary by means of filter paper until the level of the liquid in the marked capillary has reached the mark. The caps are then replaced and the filled instrument allowed to stand in the balance case for about 30 minutes and then weighed.

The drying of specific gravity bottles demands care. When glass has been heated to a high temperature, it does not necessarily regain its original volume on cooling. After cleaning the bottle with potassium dichromate and sulphuric acid, it is washed out with alcohol and ether successively and dried at a low temperature in a current of air. The use of alkaline solutions for cleaning should be avoided, and the bottle is never cooled in a desiccator.

Fig. 14.

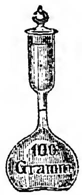


Fig. 15.

Figs. 14 and 15.—Specific Gravity Bottles.

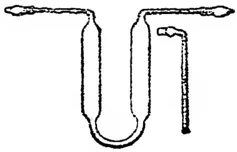


Fig. 16.—Sprengel Tube.

Determination of the Specific Gravity of Solids.—When a solid substance is heavier than and insoluble in water, its specific gravity can be determined by finding the weight of water displaced by a known weight of it, an ordinary specific gravity bottle being used for the determination. The weight of the bottle and its water content are known. A weighed quantity of the solid is put into the bottle and the latter then filled with water and weighed. Let the weight of the solid be W', that of the bottle full of water W'', and that of the bottle when it contains the solid and as much water as is required to fill it, W'''. Then :

$(W' + W'') - W'''$ is the weight of water displaced by the solid and

$\dfrac{W'}{(W' + W'') - W'''}$ is the specific gravity.

When a solid is lighter than and insoluble in water, its specific gravity may be determined by wrapping some iron or other wire round it to act as a sinker. It is not necessary to know the weight of the sinker in air, but its weight in water must be found. Let this be S. If W be the weight of the body in air and W' the weight of the body and sinker together in water, then the weight of water displaced by the body is $W + S - W'$, and the specific gravity of the body is

$$\frac{W}{W + S - W'}.$$

Specific Gravity of Textile Fibres.

Textile fibres have specific gravities of from 1·25 to 1·5, but they are not wetted readily by water and are difficult to free from air bubbles. Moreover, being colloids, they swell when placed in water. For these reasons water cannot be used in the determination of their specific gravities, but is replaced by benzene or a similar liquid, the specific gravity of which has been already determined.

Before making the determination the fibres must be degreased, washed and dried.

About one gram of the purified fibre is dried in a weighing bottle to constant weight. The dry material is introduced into the specific gravity bottle, which is about half filled with benzene. The bottle is heated on a water bath until all the air has been expelled from the fibres. The bottle and contents are then cooled, and sufficient benzene added to fill the bottle. The temperature is then adjusted, the stopper replaced and the bottle weighed.

If D_b is the specific gravity of the benzene, and W_1 the weight of the fibre, W_2 the weight of the bottle full of benzene and W_3 the weight of the bottle, fibre and benzene,

then $(W_1 + W_2) - W_3 =$ weight of benzene displaced,

$$\text{and } \frac{(W_1 + W_2) - W_3}{D_b} = \text{equivalent weight of water.}$$

$$\text{Hence} \qquad \frac{W_1 D_b}{(W_1 + W_2) - W_3} = \text{specific gravity of the fibre.}$$

It is convenient to use a specific gravity bottle with a wide mouth instead of the ordinary type.

King (*J. T. I.*, 1926, T 55) stated that the actual space taken up by a given weight of wool under various circumstances is a value which is basic to quantitative determinations such as: (1) Calculations on the diameter of fibres and yarns and on designs; (2) the quantitative relationships of fibre diameter to count and quality; (3) the accurate determination of the amounts of reagents taken up. Also (4) a complete knowledge of volume changes of fibre and yarn with regain depends upon accurate values for the specific gravity of dry wool and its variation with regain; (5) specific gravity determinations have considerable significance in connection with the degree of penetration of solvents used for wool scouring, particularly in connection with the marked difference between alcohol and benzene; (6) specific gravity determinations provide a simple method of estimating the proportions of cotton and wool in mixtures.

When a specific gravity bottle is used for the determination of the specific gravity of wool, the weight and hence the volume of the liquid displaced from the bottle by a known weight of the fibre only gives the true volume of the substance if there be no alteration in total volume when the fibre and liquid are brought together. This condition is satisfied if (*a*) the substance is entirely unaffected by the liquid, or (*b*) the volume by which the substance swells (or shrinks) is exactly equal to the volume of liquid absorbed by (or expelled from) the substance when immersed. With regard to (*b*) the swelling of ordinary wool fibre in water and various aqueous solutions and its shrinkage in glycerine are well known. It is known also that with most hygroscopic materials a contraction in total volume occurs during absorption of water, and this is probably true for sorption in general. Where this occurs, an "apparent" density will be obtained which is greater than the "true" density.

The method used by King for the determination of specific gravity was as follows :—

The wool was extracted in a Soxhlet extractor with pure alcohol. The specific gravity bottle containing the sample was dried at 102° C. under reduced pressure in an electrically-heated air bath placed in a vacuum desiccator until constant in weight. The bottle was then attached to a tube leading into the liquid to be used, contained in a pressure flask connected with the pump. Except in the case of water, drying tubes were interposed to prevent access of moisture from the pump, and the liquids employed were dried before use. The apparatus was exhausted, the pump cut off and the vacuum released slowly through the drying tubes, by which process the liquid was caused to pass into the specific gravity bottle. The procedure was repeated until the air had been completely removed. The bottle and the contents were then brought to constant temperature (25° C.).

In the case of water the true specific gravity will be given only in the case of completely saturated wool, since it is only in this case that the total volume of wool and water is unchanged on immersion of the wool. For all cases of incomplete saturation a contraction in volume takes place which results in a correspondingly higher " apparent " density.

If W = Weight of dry wool,
w = Weight of moisture originally in the wool,
w_1 = Weight of water filling bottle,
and w_2 = Weight of wool plus water filling bottle,

The apparent specific gravity of the wool, Δ_a, $= \dfrac{W \cdot \cdot w}{W + w + w_1 - w_2}$.

For a given weight of dry wool, w_2 must be the same whatever the actual regain of the wool may be at the time of its introduction into the bottle. Therefore $w_1 - w_2$ is the same for W grms. of dry wool whatever the regain may have been at the time of weighing, and $W + w_1 - w_2$ may be written W_1.

Thus the foregoing expression may be written $\dfrac{W + w}{W_1 + w}$,
and the density is greatest when $w = 0$.

The apparent density can be calculated from this by adding the weight of water corresponding to the regain to both numerator and denominator.

Apparent Density of Dry Wool in Water.—The wool was dried at 102°–103°C. in the apparatus illustrated by fig. 45, a slow current of air, finally dried over phosphorus pentoxide, being drawn through the heated tube. The apparent density of various samples varied from 1·3943 to 1·3976. It was found that wool has no sorptive capacity for benzene or toluene and that its true density is obtained in these liquids. From tests made with benzene it was concluded that the specific gravity of medulla-free wool is the same for all varieties, viz. 1·300 to 1·304; as the kempy character increases, the specific gravity diminishes, falling in the case of black face wool to 1·180.

The following applications of specific gravity determinations are used :

(1) *Determination of Regain of Wool.*—This is given by the equation

$$\Delta_A = \frac{100 + R}{71 \cdot 6076 + R},$$

where R is the regain, and Δ_A the observed apparent density in water.

(2) *Dry Wool Content.*—This, in the case of a scoured sample, is given approximately by multiplying the increase in weight of a specific gravity bottle containing water and the sample over that of the bottle with water only, by the factor 3·522.

(3) *Cotton-wool Mixtures.*—The apparent density of the dried sample is determined. Then if x be the percentage of cotton,

$$\frac{x}{100 - x} = \frac{\Delta_A - 1{\cdot}396}{1{\cdot}61 - \Delta_A}$$

(4) *Regain of Cotton.*—This can be found from the equation

$$\Delta_A = \frac{100 + R}{62{\cdot}1 + R}.$$

The Determination of Viscosity.

The viscosity of a fluid is that property which gives rise to the internal resistance offered to the motion of the fluid at any point with a velocity differing from that at an immediately adjacent point. The "*coefficient of viscosity*" of a fluid is the numerical value of the tangential force on unit area of either of two parallel planes at unit distance apart, when the space between these planes is filled with the fluid in question and one of the planes moved with unit velocity in its own plane relative to the other plane (B.E.S.A. No. 188). The C.G.S. unit of viscosity is termed a "poise," or in the case of fluids of low viscosity a "centipoise" (=0·01 poise). The viscosity of distilled water at 20° C. is practically one centipoise. The experimental determination of the tangential force would be very difficult, but certain properties of a liquid are directly connected with its viscosity, giving means of determining the latter. Among these are the time required for a given volume of the liquid to flow through a fine orifice, and the time taken by a metal sphere to sink through a vertical column of the liquid of definite depth. When these times are measured under strictly defined conditions, the viscosity of the liquid can be calculated from them.

An instrument designed to measure viscosity is termed a *viscometer*; there are two types in common use, viz. (*a*) "tube viscometers" and (*b*) "falling sphere viscometers." The tube form of viscometer is suitable for liquids the viscosities of which do not exceed 15 poises; the falling sphere type is convenient for liquids the viscosities of which are not less than 10 poises. Tube viscometers are of two kinds; the simplest type consists of a pipette with a fine orifice, and the time required by a definite volume of the liquid to flow through this orifice is measured. In the U-tube form of instrument, the liquid is allowed to flow from one limb of the tube to the other.

For many purposes the absolute viscosity of a liquid is not required, but only its viscosity compared with that of a standard liquid such as water or rape oil. When the absolute viscosity of a liquid is required, the following data are necessary: the density of the liquid and a "constant" for the particular apparatus used. The constant (K) is found by measuring under the standard conditions of experiment, the time required by a liquid of known absolute viscosity to flow from the apparatus. If t be the time of flow and d the density of the liquid under examination, and t_0, d_0 the corresponding values for a liquid of known viscosity (η_0), then the viscosity (η) of the first liquid is given by the equation

$$\eta = \eta_0 \times \frac{t\,d}{t_0\,d_0}.$$

The factor $\frac{\eta_0}{t_0\, d_0}$ is the constant K of the viscometer, and hence

$$\eta = K\, t\, d.$$

For a perfect viscometer the relation $\eta = K\, t\, d$ could be obtained from a single fluid of known density and viscosity, but, in practice, it is found that the value of K varies with the viscosity as the latter decreases. Hence, tests should be made with a series of liquids of various viscosities and the results plotted, so that the exact value of K can be seen for a liquid of any viscosity.

The following standard liquids are recommended in B.E.S.A. No. 188, 1923:

(1) Distilled water.

Temperature, . .	20° C.	25° C.
Viscosity in Centipoises,	1·005	0·894

(2) Solutions of cane sugar of 40 and 60 per cent. concentration. These solutions are prepared by dissolving 40 or 60 grms. of pure dry sucrose, respectively, in sufficient hot water to produce 100 grms. of solution. The solutions are filtered and their densities determined at 25° C., correcting for buoyancy. The viscosities of the solutions are then determined from the following formula:

Log. $\eta = \bar{1}{\cdot}95134 + 2{\cdot}9728\, x + 3{\cdot}2212\, x^2 + 24{\cdot}254\, x^3$, where η = viscosity in centipoises at 25° C., and $x = d - d_w$, d being density of solution at 25° C., and d_w density of water at 25° C., = 0·99707.

(3) A solution of pure glycerol in water at 20° C., may also be used as a standard solution, its absolute viscosity being found from the following table.

Mixture No.	Glycerol, per cent.	Sp. Gr. at $\frac{20}{20}$° C.	Approximate Viscosity at 20° C.
1	44·4	1·1129	0·046
2	57·0	1·1469	0·086
3	66·0	1·1712	0·157
4	70·6	1·1836	0·228
5	75·3	1·1963	0·350
6	80·4	1·2101	0·596
7	90·8	1·2381	2·39
8	94·8	1·2485	4·73

A series of solutions is made by weighing and mixing pure glycerol and water. The specific gravity of each mixture is determined at 20° C. The time of efflux of the mixture is then observed at this temperature, and also that of distilled water. The density (d) is obtained by multiplying the specific gravity of the mixture at $\frac{20}{20}$° C. by 0·998259, the density of water at 20° C.

Selection of Viscometer.—The type of viscometer to be used depends upon (a) the viscosity of the liquid under examination, and (b) the nature of the liquid. The limitations of tube and falling sphere instruments have been mentioned already. Another point to be considered is the possible presence of particles in suspension, which would tend to clog the orifice of a tube viscometer. Starch solutions, for example, are best dealt with by a falling sphere instrument.

Tube Viscometers.—The standard tube viscometers of the B.E.S.A. are of two kinds, viz., co-axial bulb viscometers and U-tube viscometers. In either case the tube should be such that the time of flow is not less than 60 seconds and preferably not less than 100 seconds. The length of the capillary should be 10 cm. and the diameter depends upon the kinematic viscosity, *i.e.*,

$$\frac{\text{Viscosity } (\eta) \text{ in poises}}{\text{Density } (d) \text{ in grms. per c.c.}}$$

Details of the standard types and dimensions may be found in B.E.S.A. Specification No. 188, 1923.

A standard U-tube viscometer is shown in fig. 17. It is filled from the marks *A* to *B* with the liquid under test, the final adjustment being made after the apparatus has attained the desired temperature by

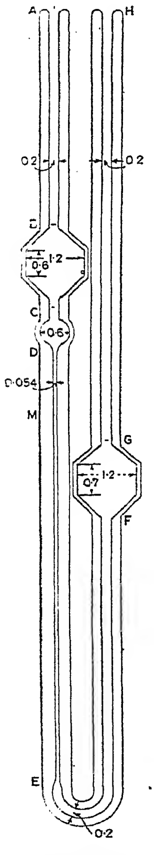


Fig. 17.—Standard U-Tube Viscometer.

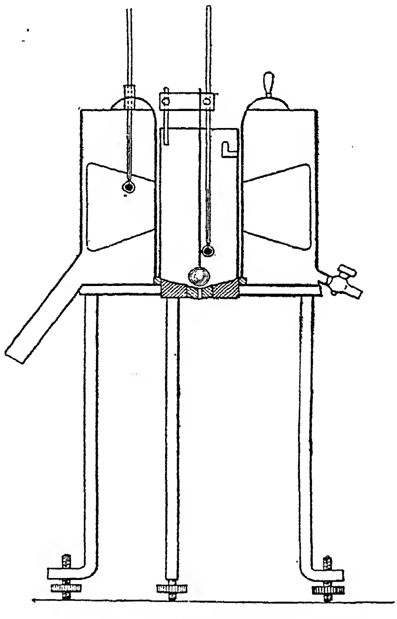


Fig. 18.—Redwood's Viscometer.

immersion in a thermostat. The tap or pinch-cock is then opened and the time of passage of the liquid from *C* to *D* is determined by means of a stop watch.

In addition to viscometers of the bulb type, there are many other recognised forms of instruments amongst which is that of Redwood, used very largely for oils. The Saybolt viscometer is used in America and the Engler in Germany,

whilst a special type is employed by the American National Association of Glue Manufacturers.

The Redwood Viscometer.—This apparatus (fig. 18) is used very largely for

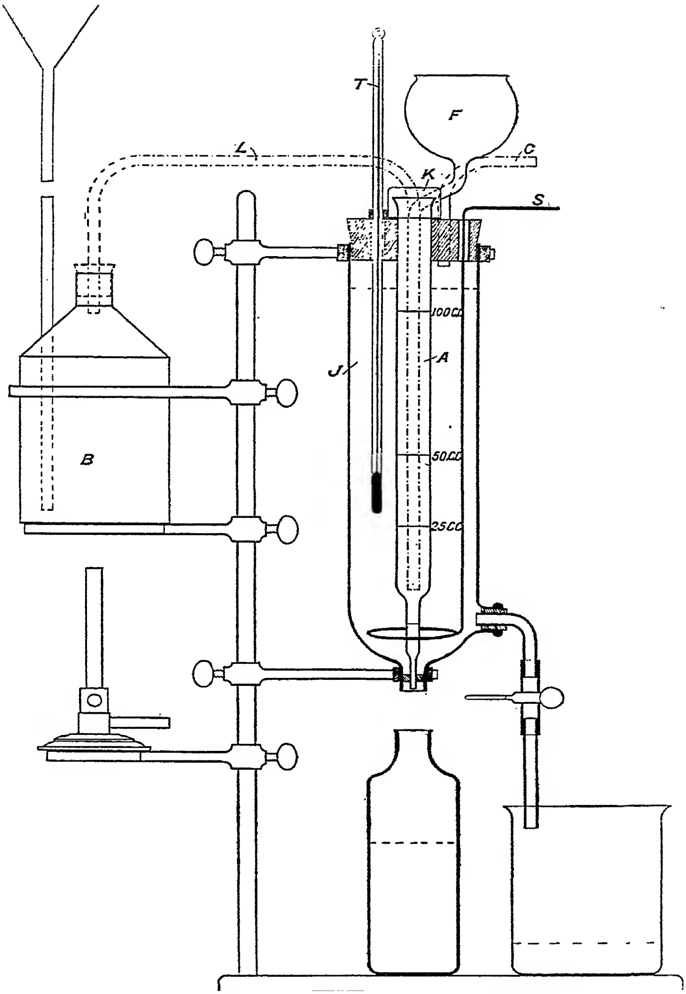


Fig. 19.—Coleman-Archbutt Viscometer.

the determination of the viscosity of lubricating and other oils. A metal cylinder serves as a pipette for containing the oil. At the bottom of the cylinder is a small orifice which can be closed by means of a metal sphere attached to a thin rod.

The cylinder stands in a copper bath which is filled with water or oil and can be heated by means of a flame applied to the projecting arm. The bath is provided with mechanical stirring apparatus and a thermometer, a second thermometer being suspended in the oil. The liquid to be tested is heated to the desired temperature and poured into the cylinder, the water-bath also being at the same temperature. When the exact temperature has been attained, the level of the oil is adjusted by raising the metal plug and allowing some to run out, until it just reaches the top of the pointer. A graduated 50-c.c. flask is then placed beneath the orifice, the plug is removed, and the time taken for exactly 50 c.c. of

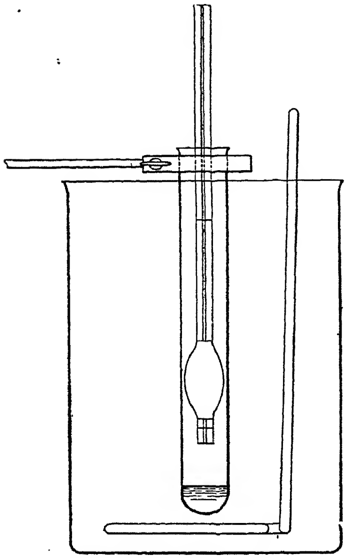


Fig. 20.—Seaber Viscometer.

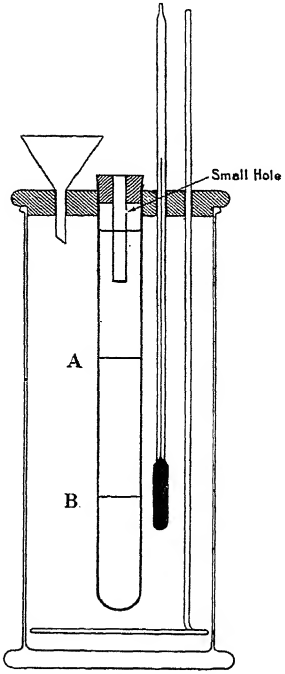


Fig. 21.—Falling Sphere Viscometer.

:he oil to run out is recorded with a stop-watch. This number is generally ·aken as a measure of the viscosity of the sample, being known as " seconds Redwood " or " Redwood viscosity."

The Coleman-Archbutt Viscometer.—The Coleman-Archbutt viscometer :onsists of a glass burette (fig. 19) contained in an outer vessel in which water is ılaced. A stirrer is provided and the temperature of the water can be adjusted ıy means of steam. The tube and orifice are cleaned and dried, and the orifice losed by means of a small pointed wooden peg. The jacket is filled with water t the required temperature, the liquid to be tested is heated to the temperature f the test and poured into the burette to a height of about half an inch above he 100 c.c. mark. The liquid is then stirred carefully with a thermometer until ; has acquired the correct temperature. The thermometer is then removed and

after the liquid has become stationary, the peg is removed and the time required by the liquid to flow from the upper to the zero mark is measured with a stop watch.

For comparative purposes, a viscometer can be constructed from any pipette, provided that it has a capillary orifice ground-off perfectly horizontal. That shown in fig. 20 is described by Seaber (*Industrial Chemist,* 1926, 244). It consists of a small pipette blown from thermometer tubing. The liquid to be tested is placed in the test tube, the latter being immersed in a beaker containing water and provided with a stirrer. The liquid is drawn up into the pipette and the time of efflux between two marks is measured. A very similar apparatus known as the Klever viscometer has been described by Günther (*Chem. Zeit.*, 1927, **51**, 526).

Falling Sphere Viscometers.—This type of viscometer is used for liquids which are liable to clog the orifice of the capillary or tube viscometer. An instrument of this kind is shown in fig. 21, reproduced from the B.E.S.A. specification referred to before.

The following rules for construction are given by the B.E.S.A. (*loc. cit.*) :

(1) The maximum diameter of the sphere to be used shall be determined from the formula

$$\eta = \frac{d^2}{18}(\sigma - \rho)\frac{g}{v}$$

where η is the approximate viscosity in poises, d the diameter of the sphere in cm., σ and ρ the density (grms./c.c.) of the sphere and of the liquid, respectively, $g = 981$, and v the velocity of fall (cm./sec.). The following table gives the maximum size of ball which can be used for a liquid of definite viscosity.

Diameter of Ball.	Viscosity in Poises.	Diameter of Ball.	Viscosity in Poises.
$\frac{1}{16}$ in.	10	$\frac{1}{4}$ in.	170
$\frac{3}{32}$,,	25	$\frac{3}{8}$,,	380
$\frac{1}{8}$,,	40	$\frac{1}{2}$,,	680
$\frac{3}{16}$,,	100	$\frac{3}{4}$,,	1500

(2) The tube used must have a diameter at least ten times that of the falling sphere and its length must be twice that over which the fall of the sphere is to be timed.

The liquid to be tested is heated to the required temperature and introduced into the tube, which is placed vertically in the bath, a plumb-line being used as a guide. The sphere is then introduced through the small hole and the time taken to fall between A and B is observed. The absolute viscosity is calculated from the formula

$$\eta = \frac{td^2(\sigma - \rho)g}{18s\left(1 + 2{\cdot}4\frac{d}{D}\right)\left(1 + \frac{5d}{3h}\right)}$$

where g = 981 cm./sec.^{2},
d = diameter of sphere in cm.,
σ = density of sphere in grms. per c.c.,
ρ = density of liquid under test in grms. per c.c.,
t = time in seconds taken for the sphere to fall through the distance s cm., between the two reference marks,
D = diameter of tube in cm.,
h = height of column of liquid in cm.

The falling sphere viscometer can of course be used for comparative tests, the following formula being applied:

$$\frac{\eta_1}{\eta_2} = \left(\frac{\sigma - \rho_1}{\sigma - \rho_2}\right) \left(\frac{t_1}{t_2}\right)$$

where the suffixes 1 and 2 refer to the liquid being tested and the comparison liquid, respectively. The tests should be carried out with the same tube and sphere.

The following table for the approximate conversion of Redwood, Saybolt and Engler times into each other is taken from the *Industrial Chemist*. For any particular "Redwood time" the factor corresponding to the nearest time given in the table is chosen.

Redwood Viscosity.	Redwood into Saybolt.	Redwood into Engler.	Saybolt into Engler.
	Multiply by	Multiply by	Multiply by
21·5	1·51	2·61	1·73
30	1·12	1·93	1·72
40	1·14	1·88	1·65
50	1·15	1·86	1·61
60	1·16	1·83	1·58
70	1·17	1·81	1·56
100	1·17	1·80	1·53
200	1·18	1·77	1·50
300 and over	1·18	1·77	1·50

CHAPTER IV.

STANDARD VOLUMETRIC SOLUTIONS.

THE standard solutions used in volumetric analysis contain a definite weight of the reagent per litre of water or other solvent. In order that different standard solutions may be comparable with one another, their concentrations should have some simple relationship to the molecular weight of the dissolved substance. The method adopted is that one litre of the normal standard solution shall contain one gramme of replaceable hydrogen or its equivalent of the reacting element or group ; a solution made up in this manner is termed a *Normal Solution*, abbreviated to the letter *N*. Dilutions made from the normal solution are known as decinormal ($N/10$), centinormal ($N/100$), etc. In the case of acids, a normal solution is made according to the definition by dissolving in one litre of water such a weight of the acid as will contain 1 gramme of replaceable hydrogen. This is determined by the basicity of the acid. Thus in the case of hydrochloric acid the requisite quantity is one gramme-molecular weight, whilst in the case of sulphuric acid it is half a gramme-molecular weight. The reactive constituent of an inorganic base is the hydroxyl group. Hence, according to the definition, a normal solution of a base contains one gramme-molecular weight of replaceable hydroxyl per litre. In the case of sodium hydroxide one gramme-molecule is required, and half a gramme-molecule in the case of barium hydroxide. In other cases the quantity to be taken for one litre of a normal solution is determined by the chemical reaction which takes place. Thus the reaction of sodium thiosulphate with iodine is expressed by the equation

$$2\,Na_2S_2O_3 + I_2 = 2\,NaI + Na_2S_4O_6.$$

Since two molecules of sodium thiosulphate react with two atoms of iodine, one gramme-molecular weight will contain the equivalent of one gramme of hydrogen. The necessary weight of oxidising agents such as potassium permanganate depends upon the amount of available oxygen which they contain. Thus, two molecules of potassium permanganate ($KMnO_4$) yield five atoms of oxygen, which are equivalent to ten atoms of hydrogen. Hence the quantity of potassium permanganate required to contain the equivalent of one gramme of hydrogen is one-fifth of a gramme-molecule.

Stock Solutions.

Stock solutions are conveniently prepared of normal or double normal strength, the volume made depending upon the daily requirements and the stability of the solution. In the preparation of stock solutions the required amount of substance should be dissolved in distilled water and the solution diluted in a marked litre flask so that the volume when measured at 15° C. is exactly 1 litre. It is not always convenient from the point of view of time to carry out the preparation of a standard solution at 15° C. Laboratory temperatures are

generally higher than this, so that the volume of a solution prepared at room temperature will be less than 1 litre at 15° C. If α is the coefficient of cubical expansion of glass and β the coefficient of cubical expansion of the solution, the volume of a solution whose temperature is θ° C. after finally diluting to the mark will be

$$1000 \times \frac{1 + (\theta - 15)\,\alpha}{1 + (\theta - 15)\,\beta} \text{ c.c.}$$

if the temperature is brought to 15° C.; and similarly for other temperatures.

The following table by Schlösser (*Chem. Zeit.*, 1904, 4; 1905, 510) gives the number of cubic centimetres of water at 15° C. which must be added to one litre of standard solutions at temperatures above 15° C. in order that the strengths of the solutions may be correct on cooling to 15° C.

Temperature.	Water and 1/10 *N* Solutions.	1/1 *N* HCl.	1/1 *N* $H_2C_2O_4$.	1/1 *N* H_2SO_4.	1/1 *N* HNO_3.	1/1 *N* Na_2CO_3.	1/1 *N* NaOH.
15	0·00	0·00	0·00	0·00	0·00	0·00	0·00
16	+ 0·13	+ 0·18	+ 0·20	+ 0·24	+ 0·25	+ 0·24	+ 0·25
17	0·27	0·36	0·40	0·49	0·50	0·49	0·51
18	0·42	0·56	0·61	0·75	0·76	0·75	0·78
19	0·59	0·76	0·82	1·02	1·03	1·02	1·05
20	0·76	0·97	1·05	1·30	1·30	1·29	1·33
21	0·95	1·19	1·29	1·58	1·58	1·57	1·62
22	1·14	1·41	1·54	1·86	1·87	1·85	1·92
23	1·35	1·64	1·80	2·15	2·17	2·14	2·23
24	1·56	1·88	2·07	2·45	2·47	2·44	2·54
25	1·79	2·14	2·34	2·76	2·78	2·75	2·85
26	2·02	2·40	2·62	3·08	3·10	3·06	3·17
27	2·27	2·67	2·90	3·41	3·43	3·38	3·50
28	2·52	2·95	3·19	3·75	3·76	3·70	3·83
29	2·75	3·23	3·49	4·09	4·10	4·04	4·19
30	3·06	3·52	3·82	4·43	4·44	4·38	4·52

The application of the table is indicated by the following examples: A normal solution of sulphuric acid is prepared in a litre flask graduated to contain 1000 c.c. at 15° C. The final temperature of the solution on making up to the mark is 22° C. From the table it is seen that a further 1·86 c.c. of water must be added to compensate for the excess temperature over 15° C. in order that the normality of the solution may be correct at the standard temperature.

If the conditions are such as would result in the temperature of the solution being less than 15° C., the water used should be heated to a temperature slightly higher than 15° C.

Normal Sulphuric Acid.—About 27 c.c. of pure concentrated sulphuric acid, *i.e.*, approximately 50 grammes, are poured slowly and with constant agitation into a litre flask containing about 500 c.c. of distilled water. The solution is then cooled to 15° C., and diluted to 1 litre with distilled water.

The exact strength of the solution is determined by titration with sodium carbonate solution. About 2 grms. of the pure salt are heated carefully in a platinum dish over a small Bunsen flame until constant weight is obtained. Care must be taken to avoid fusing the carbonate or carbon dioxide may be given off. The weighed salt is dissolved in distilled water, a drop of methyl orange added and the acid run in from a burette until the carbonate solution is nearly neutralised. The solution is then boiled gently for about three minutes, to expel

carbon dioxide, cooled and the titration completed. From the volume of acid used, its exact strength can be calculated, since 1 c.c. of normal acid corresponds to 0·053 grm. of pure sodium carbonate. Thus, if 2·150 grms. of sodium carbonate were weighed out, the volume of exactly normal sulphuric acid required for neutralisation would be $\frac{2 \cdot 150}{0 \cdot 053}$ c.c., *i.e.*, 40·57 c.c.

Hence if 39·65 c.c. of the acid solution are required for neutralisation, this volume of the acid is equivalent to 40·57 c.c. of normal sodium carbonate solution, and the acid is too strong. In order to make it exactly normal each 39·65 c.c. must be diluted to 40·57 c.c., *i.e.*, 0·92 c.c. of water must be added. Hence the volume of water to be added to one litre is

$$\frac{0 \cdot 92}{39 \cdot 65} \times 1{,}000 = 23 \cdot 2 \text{ c.c.}$$

It is convenient to use a flask with two graduations, at 1000 c.c. and 1100 c.c. respectively, and make up 1100 c.c. of the solution. After standardising, solution is removed by means of a pipette until exactly 1000 c.c. remain, to which the required volume of water can be added.

If chemically pure sodium carbonate is not available, some sodium hydrogen carbonate (sodium bicarbonate) is washed with cold distilled water, dried, transferred to a platinum crucible and heated to about 275° C. until it is completely converted into carbonate. The carbonate is then transferred to a stoppered weighing bottle while still hot, and cooled in a desiccator over calcium chloride.

Normal Hydrochloric Acid.—"Commercially pure" hydrochloric acid has a specific gravity of 1·16, corresponding to 32 per cent. of real acid. If 120 c.c. are diluted to one litre a solution slightly stronger than normal will be obtained. The exact strength may be determined against a weighed quantity of pure sodium carbonate as described for normal sulphuric acid, except that the solution cannot be boiled during titration. When an accurately standardised solution of sodium hydroxide is available this may be used advantageously for the standardisation. An exact method is to treat 25 c.c. of the acid with an excess of silver nitrate, boil the mixture to coagulate the precipitated silver chloride, which is then filtered off on a Gooch crucible, washed, dried and weighed. Another method which is employed sometimes is as follows: A piece of Iceland spar is weighed and placed in a beaker. Some distilled water is added and then 25 c.c. of the acid to be standardised. The beaker is allowed to stand on the top of a drying oven until no more calcium carbonate is dissolved. The Iceland spar is then removed, washed with distilled water, dried and weighed. The loss of weight gives the weight of hydrochloric acid in the 25 c.c. used, since 100 parts of Iceland spar will neutralise 73 parts of acid.

Normal Nitric Acid.—"Pure" nitric acid has a specific gravity of 1·5 and contains 94 per cent. of acid. A normal solution contains 63 grammes per litre, and about 67 grammes of the pure acid or 45 cubic centimetres are required for one litre. The solution is standardised in the same manner as sulphuric acid.

Sodium Hydroxide Solution.—In the ordinary way the preparation of normal solutions of sodium hydroxide is carried out as follows: 45 grms. of stick caustic soda are weighed out. The carbonate on the surface of the sticks is removed as far as possible with a jet of water from a wash bottle and the washed sticks dissolved in 1050-1100 c.c. of distilled water. The solution is allowed to stand until cool, and then titrated against a standard acid solution, using methyl orange as indicator. Thus, if 50 c.c. of normal acid require 49·8 c.c. of the

caustic soda solution for neutralisation, it is apparent that each 49·8 c.c. of the caustic alkali must be diluted with 0·2 c.c. of water to make the solution exactly normal. After carrying out the dilution of the bulk in this manner, the diluted solution should again be titrated, as a check.

Sodium hydroxide solutions prepared in the foregoing manner always contain carbonate and are not, therefore, suitable for titrations in which phenolphthalein is to be employed as indicator, unless the carbonate actually present is determined and allowed for. A solution of sodium hydroxide free from carbonate may be made by dissolving freshly cut and cleaned metallic sodium in carbon dioxide-free water. The sodium may be dissolved first in a little alcohol, the sodium ethoxide which is formed being decomposed with carbon dioxide-free water, the solution boiled until the alcohol has been expelled, and then diluted. Another method of preparation is to boil with water equivalent quantities of pure barium hydroxide and sodium sulphate. The mixture is transferred, without cooling, to a stoppered litre flask and diluted to the mark with boiling distilled water. After allowing the barium sulphate which is formed to settle, the clear liquid is tested for barium and sulphates, and these removed, if present, by the careful addition of sulphuric acid or barium hydroxide.

Decinormal Sodium Carbonate Solution.—About 6 grammes of pure sodium carbonate are placed in a platinum dish and heated gently on a hot plate until constant in weight. Exactly 5·3 grms. of the dried substance are weighed in a stoppered weighing bottle, dissolved in water, the solution washed into a litre flask and diluted to the mark with distilled water.

Potassium Permanganate.—Potassium permanganate gives up oxygen in the presence of sulphuric acid in accordance with the equation $2\,KMnO_4 + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O$. Hence 316 grammes of potassium permanganate yield five gramme-atoms of oxygen, equivalent to ten of hydrogen. In order, therefore, to obtain a solution containing the equivalent of 1 gramme of hydrogen per litre, one-fifth of a gramme-molecule (31·6 grms.) must be taken, or 3·16 grms. for a decinormal solution. About 6·5 grms. of the salt are weighed out and dissolved in water. The solution is made up to 2 litres and allowed to stand 8–14 days before standardising, or using. This period is necessary to allow complete oxidation of the organic matter always found present in distilled water to occur. When this oxidising process is completed, the solution is perfectly stable if protected from dust and reducing vapours.

The standardisation of permanganate solutions is best effected against a solution of oxalic acid (*q.v.*). 25 c.c. of a tenth-normal solution of oxalic acid are pipetted into a litre conical flask and 10 c.c. of dilute (1 : 4) sulphuric acid added, the mixture diluted to about 200 c.c. with distilled water at a temperature of 70° C. and titrated with the permanganate solution. The end-point of the titration is reached when the addition of one more drop of permanganate produces a permanent pink coloration in the titrated liquid.

Since $2\,KMnO_4$ molecules give up 5 atoms of oxygen and 5 atoms of oxygen oxidise $5\,(COOH)_2$ molecules, any volume of decinormal oxalic acid is exactly equivalent to the same volume of decinormal potassium permanganate solution.

Pure ferrous ammonium sulphate, $FeSO_4 . (NH_4)_2SO_4 . 6\,H_2O$, is used also for the standardisation of potassium permanganate solution. About 1 grm. of the substance is weighed, dissolved in water containing sulphuric acid and the permanganate solution run in from a burette until a faint pink permanent colour is obtained. Each cubic centimetre of $N/10$ permanganate solution will oxidise 0·039216 grm. of ferrous ammonium sulphate.

Potassium Dichromate.—Potassium dichromate, like the permanganate salt, is an oxidising agent and is employed in a similar manner to the perman-

ganate. From each molecule of the salt three atoms of oxygen are available for oxidation, thus

$$K_2Cr_2O_7 + 4\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3O.$$

That is to say 294 grms. of potassium dichromate yield 48 grms. of oxygen available for oxidation. A normal solution of potassium dichromate will therefore contain $\frac{294}{6} = 49$ grms. of the salt per litre.

To prepare a standard solution of potassium dichromate a little more than the actual required quantity of the salt is weighed out and fused in a porcelain basin. On cooling, the product is ground to a fine powder, dissolved in water and made up to volume. The solution so prepared is standardised with sodium thiosulphate, in the manner to be described. When A.R. dichromate is used standardisation is, however, unnecessary.

Sodium Thiosulphate.—A decinormal solution of sodium thiosulphate contains 24·83 grms. of the crystalline salt, $Na_2S_2O_3 \,.\, 5\,H_2O$, per litre.

In preparing a standard solution of sodium thiosulphate great care must be taken to prevent the access of carbon dioxide to the prepared solution, and materials which are free from carbon dioxide, or carbanion, $CO_3^{=}$, must be employed. Under the action of carbonic acid the free thio-acid is liberated, and in consequence of its instability, this breaks down into sulphurous acid and free sulphur, thus

$$Na_2S_2O_3 \quad \cdot\, 2\,H_2CO_3 = 2\,NaHCO_3 + H_2S_2O_3,$$
$$H_2S_2O_3 = H_2SO_3 + S.$$

When all the $CO_3^{=}$ present in solution has been used up, solutions of sodium thiosulphate may be kept for months without undergoing any appreciable change in concentration.

The stock solution of sodium thiosulphate should be of the concentration used in the determination in which it is to be employed. For decinormal solutions 25 grms. of the crystalline salt are weighed out for each litre of solution to be prepared. The water employed in dissolving the salt should be recently-boiled distilled water, and after solution is complete the thiosulphate should be kept for 8–14 days before standardisation.

The standardisation of sodium thiosulphate solutions is most readily carried out by titration against a standard solution of potassium dichromate, in the following manner: 25 c.c. of decinormal potassium dichromate solution are pipetted into a conical titrating flask, diluted with water to about 200 c.c. and about 2 grms. of potassium iodide added, followed by 5 c.c. of concentrated hydrochloric acid. The hydrochloric acid is oxidised by the dichromate and the liberated chlorine sets free its equivalent of iodine from the potassium iodode. The liquid becomes dark brown in colour and contains the equivalent of 25 c.c. of tenth-normal iodine solution. The thiosulphate solution is now run in from a burette, the colour of the titrated solution becoming lighter as the iodine reacts with the sodium thiosulphate, and when only a very faint yellow colour remains, 1–2 c.c. of starch solution are added. This produces a deep coloration comprising the brown due to free iodine, the blue of the starch-iodine compound formed, and the green of chromium chloride. The titration is continued drop by drop until the yellowish colour first disappears, and then the blue also: the end-point of the titration is the point at which the blue coloration is replaced by a pure green colour.

It should be noted that unless the solution is diluted well, the green colour

of the chromium chloride may make the end-point difficult to see. Sulphuric acid may be used instead of hydrochloric acid, but more is necessary. Treadwell states that in very dilute solutions of sulphuric acid the reaction only takes place very slowly.

Iodine.—The usefulness of iodine solution in volumetric analysis depends largely upon its reaction with sodium thiosulphate, the iodine combining with part of the sodium, thus,

$$2\,Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2\,NaI.$$

With starch solution iodine yields an intensely blue compound usually denoted by the term "starch-iodide." On adding a solution of sodium thiosulphate to a starch-iodide solution the colour is discharged when the amount of thiosulphate added is just equivalent to the iodine present in solution.

If iodine be considered as an oxidising agent, reacting in accordance with the equation

$$I_2 + H_2O = 2\,HI + O,$$

then 127 grms. of iodine yield one gramme-equivalent of oxygen. A normal solution of iodine will therefore contain 127 grms. and a tenth-normal solution 12·7 grms. of iodine per litre. A large-bulk stock solution of iodine should not be prepared, since the concentration decreases comparatively rapidly in consequence of volatilisation of the solid from aqueous solution, and its slow reaction with water. 12·7 grms. of the purest resublimed iodine should be dissolved in water containing 20 grms. of potassium iodide and the solution made up to one litre. This tenth-normal solution should be kept in the dark in a well-stoppered bottle and standardised at regular intervals with sodium thiosulphate solution.

To standardise the iodine solution 25 c.c. are pipetted into a flask and standardised tenth-normal sodium thiosulphate solution run in until the liquid becomes straw coloured. 1–2 c.c. of starch solution are then added and the titration continued drop by drop until the blue coloration just disappears. The factor for the solution is then calculated in similar manner to the case of acids and alkalis.

Starch Solution.—The preparation of the starch solution employed in iodine titrations is carried out in the following manner: About 1 grm. of soluble starch is rubbed into a cream with a little cold water and added to 100 c.c. of boiling distilled water with constant stirring. The solution should be made up frequently since its sensitiveness is considerably affected by acid fumes and bacteria.

Arsenious Acid.—4·95 grms. of arsenic trioxide (of the quality known as "analytical reagent") are accurately weighed out into a porcelain basin and dissolved by gently warming with a little concentrated sodium hydroxide solution. When solution is complete the liquid is transferred to a graduated litre flask and the porcelain basin well rinsed out into the flask. A drop of phenolphthalein solution is now added and then dilute sulphuric acid until the phenolphthalein is just decolorised. 500 c.c. of a filtered 4 per cent. solution of sodium bicarbonate are then added, and if the solution reacts alkaline, as indicated by the phenolphthalein present, a further quantity of sulphuric acid is added until the liquid is again just decolorised. The solution is then made up to volume. The approximately tenth-normal arsenious acid prepared in this manner is standardised against iodine in the manner described for sodium thiosulphate.

Oxalic Acid.—A decinormal solution of oxalic acid may be made by dissolving exactly 6·303 grms. of the pure crystalline acid, $H_2C_2O_4 . 2 H_2O$, in water and making the solution up to one litre. No standardisation is necessary, oxalic acid being used often as the starting point for the preparation of standard acids and alkalis. The strength may be checked when desired by titration with decinormal sodium hydroxide solution in the presence of phenolphthalein, or with decinormal potassium permanganate solution (*q.v.*).

Silver Nitrate.—Decinormal silver nitrate solution is made by dissolving 17 grms. of pure silver nitrate in water and diluting the solution to one litre.

Potassium Sulphocyanide (or *Ammonium Sulphocyanide*).—Both of these salts are hygroscopic and cannot be weighed accurately. In order to prepare decinormal solutions, approximately 10 grms. of the potassium salt or 9 grms. of the ammonium salt are dissolved in a litre of water and the solution standardised by means of decinormal silver nitrate solution. A cold saturated solution of ferric alum is required as indicator, to which has been added just enough nitric acid to discharge the brown colour. From 1 to 2 c.c. of this solution are used for 100 c.c. of the silver nitrate solution. The titration is carried out as follows: 20 c.c. of decinormal silver nitrate solution are placed in a beaker, diluted to 50 c.c. with water and 1 c.c. of the indicator added. The sulphocyanide solution is then run in from a burette, with constant stirring, until a permanent red colour is produced, due to the formation of ferric sulphocyanide:

$$AgNO_3 + KCNS = KNO_3 + AgCNS,$$
$$Fe_2(SO_4)_3 + 6KCNS = Fe_2(CNS)_6 + 3\,K_2SO_4.$$

In the titration of chlorides the red colour is permanent only in the presence of excess of sulphocyanide, owing to decomposition of the silver salt in accordance with the equation

$$6\,AgCl + Fe_2(CNS)_6 = 6\,AgCNS + Fe_2Cl_6.$$

This difficulty can be avoided by back-titration. A measured volume of the chloride solution is placed in a graduated stoppered flask and a known excess of $N/10$ silver nitrate added. The mixture is then acidified with nitric acid, the stopper inserted and the flask shaken until the silver chloride has coagulated. The mixture is now made up to a definite volume, well shaken and filtered. The first 10 c.c. of the filtrate are rejected and an aliquot portion of the remainder titrated with the potassium sulphocyanide solution in the presence of ferric alum.

Voteck's Mercuric Nitrate Solution.—This solution is useful for the determination of chlorides in coloured liquids. It is made by dissolving a weighed quantity of mercury in a slight excess of nitric acid. The estimation depends upon the formation of a soluble double compound having the formula $Hg(NO_3)_2 . 2\,MCl$, each atom of mercury corresponding to two of chlorine. The solution to be titrated is made slightly acid with nitric acid, 0·06 grm. of sodium nitroprusside added as indicator, and the mercuric nitrate solution run in until a faint permanent turbidity due to mercuric nitroprusside is produced. The solution should be standardised against pure sodium chloride. The method cannot be used in the presence of sulphides, sulphites or nitrites.

Potassium Bromate Solution.—The use of potassium bromate solution depends upon the reaction

$$5\,KBr + KBrO_3 + 6\,HCl + = 6\,KCl + 6\,Br + 3\,H_2O.$$

Hence a decinormal solution may be made by dissolving 2·783 grms. of the salt in one litre of water. The solution is standardised in the following manner:

A suitable volume (25 c.c.) is pipetted into a stoppered bottle, diluted to 200 c.c. with water, and 5 grms. of potassium or sodium bromide (free from bromate), 5 grms. of potassium iodide (free from iodate) and 5 c.c. of chlorine-free hydrochloric acid added. The liberated iodine is then titrated with decinormal sodium thiosulphate solution.

If preferred, the solution may be prepared with potassium bromate and bromide in the proportions required by the foregoing equation. Suitable proportions are 5·566 grms. of potassium bromate and 19·83 grms. of potassium bromide in one litre. In this case only hydrochloric acid and potassium iodide are added when standardising.

Titanous Chloride Solution.—Titanous chloride, $TiCl_3$, is oxidised readily to $TiCl_4$, and is thus a powerful reducing agent. Its use in volumetric analysis is due chiefly to Knecht and Hibbert (*New Methods in Volumetric Analysis*). The solution must be kept in contact with hydrogen to prevent it becoming oxidised, and must be standardised frequently. The titration is carried out in the presence of an inert gas such as carbon dioxide. The following details are given by Knecht and Hibbert:

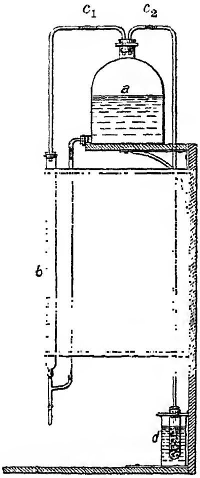


Fig. 22.—Apparatus for Titrating with Titanium Chloride.

Preparation of Solution.—50 c.c. of commercial (20 per cent.) titanous chloride solution are boiled for a minute with 100 c.c. of concentrated hydrochloric acid in a small flask, the solution cooled, and made up to about $2\frac{1}{2}$ litres with air-free water. The solution is placed in an aspirator, *a* (fig. 22), which it should nearly fill. The aspirator is connected with a burette, *b*, and a hydrogen-generating apparatus, *d*. At c_1 and c_2 are bead valves inside rubber tubing connections. The inner tube of *d* contains zinc and the outer a mixture of equal volumes of water and hydrochloric acid; at the bottom of the tube containing the zinc is a small aperture for the entrance of the acid. When the valve c_2 is opened the acid attacks the zinc, the hydrogen thus liberated keeping the apparatus free from air.

Standardisation.—Either ferric alum or ferrous ammonium sulphate is used. In the former case about 14 grms. of ferric alum are dissolved in dilute sulphuric acid and the solution made up to one litre with distilled water. 25 c.c. of this solution are placed in a flask, together with a little potassium sulphocyanide solution as indicator. The titanous chloride solution is then run in until the red colour due to the ferric sulphocyanide just disappears, indicating that all the ferric salt has been reduced. Since the exact amount of ferric iron taken is known, the strength of the titanous chloride solution can be calculated in terms of the iron which it reduces.

When ferrous ammonium sulphate is used, 3·5 grms. of the salt are dissolved in water, 100 c.c. of $5N$ sulphuric acid added and the solution made up to 250 c.c. A measured volume of this solution (*e.g.* 25 c.c.) is placed in a flask and $N/50$ potassium permanganate solution run in until a faint pink colour is produced. A little potassium sulphocyanide solution is then added and the ferric iron titrated with the titanous chloride solution, the end-point being indicated by the disappearance of the red colour:

$$2\,TiCl_3 + 3\,H_2SO_4 + Fe_2(SO_4)_3 = 2\,FeSO_4 + 2\,Ti(SO_4)_2 + 6\,HCl.$$

If 25 c.c. of the ferrous ammonium sulphate solution requires 26·3 c.c. of the titanous chloride solution, then

$$1 \text{ c.c. } TiCl_3 \text{ solution} \equiv 0{\cdot}001901 \text{ grm. Fe.}$$

The chief difficulty in connection with the method is the instability of titanous chloride solution, constant re-standardisation being required. Wilkinson and Tyler (*J. Soc. Dyers and Col.*, 1927, 115) found that titanous sulphate solution is comparatively stable and that zinc amalgam forms a convenient reducing agent for the solution. They recommend the following form of apparatus (fig. 23). A store bottle, *A*, is connected to a burette, *D*, by a glass tube, *B*, provided with a pinch cock, *C*. The neck of the bottle is closed with a rubber bung, a hole

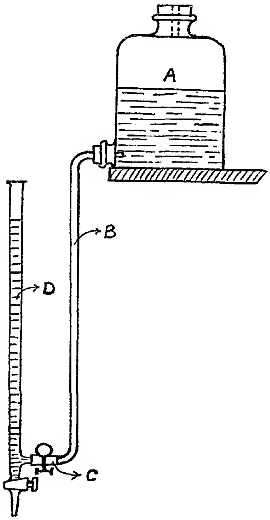


Fig. 23.—Wilkinson and Tyler's Apparatus.

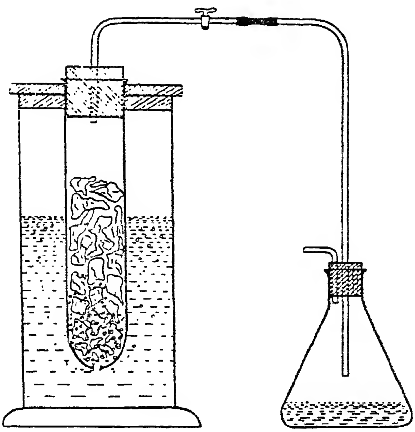


Fig. 24.—Titration Flask for Titanium Chloride Titrations.

in which is plugged loosely with glass wool. One and a half litres of *N*/4 sulphuric acid are placed in the container and zinc amalgam is distributed evenly over the bottom. A layer of naphtha is run in over the surface of the liquid. 30 c.c. of commercial titanous solution are placed in a flask and diluted to 200 c.c. with *N*/4 sulphuric acid. Some zinc amalgam is added and the flask is closed with a rubber bung provided with two holes for the passage of carbon dioxide. The solution is heated, carbon dioxide being passed through, until a clear violet colour is produced; it is then cooled and added to the stock bottle.

Callan and Henderson (*J.S.C.I.*, 1922, 161 T) recommend the use of *p*-nitro-aniline in the standardisation of titanous chloride solution. This substance is reduced in accordance with the equation

$$C_6H_4{<}^{NH_2}_{NO_2} + 6\,TiCl_3 + 6\,HCl = 2\,H_2O + 6\,TiCl_4 + C_6H_4{<}^{NH_2}_{NH_2}$$

Titrations with Titanous Chloride Solution.—Either direct or indirect methods employed. Compounds which are coloured, but form colourless reduction pro-cts or leuco-compounds, can be titrated directly. In many cases no definite l-point can be obtained and indirect titration must be made use of. An excess the titanous chloride solution is added, the mixture boiled, and the unused inous chloride determined by back titration with standard iron alum solution, assium sulphocyanide being use as indicator. As mentioned already, titrations carried out in an atmosphere of carbon dioxide; apparatus suitable for this llustrated in fig. 24. In the case of dyestuffs which are precipitated from ir aqueous solutions by acids, an excess of Rochelle salt is added to the ution before titration.

Fehling's Solution.—This solution is used in the determination of sugars l other reducing agents, such as oxycellulose. Two solutions are required, ich are mixed in equal volumes just before use; they are (1) 34·63 grms. of stalline copper sulphate dissolved in 500 c.c. of water, (2) 70 grms. of stick ium hydroxide and 173 grms. of Rochelle salt dissolved in 500 c.c. of water. her a volumetric or gravimetric method of analysis may be used. In the umetric method the solution of the sugar is placed in a burette and 10 c.c. of ıling's solution are pipetted into a small flask and diluted with 10 c.c. of water. e flask is placed upon an iron plate and the contents boiled gently. The sugar ıtion is run in from the burette a little at a time, the solution in the flask ng brought to the boiling point after each addition. When all the Fehling's ıtion has been decomposed, the supernatant liquid after allowing the cuprous de to settle will show no traces of blue colour. The volume of the sugar ıtion used is then read off and the quantity of sugar calculated from the owing factors:

Sugar.	Weight Oxidised by 10 c.c. of Standard Fehling's Solution.
Dextrose, . .	0·0500 grm.
Levulose, . .	0·0500 ,,
Invert sugar, . .	0·0500 ,,
Lactose, . . .	0·0678 ,,
Maltose, . . .	0·0807 ,,

e recognition of the end-point is not difficult, but may be assisted by the use ın external indicator. Harrison's indicator is made by boiling 0·05 grm. tarch with a little water, adding 10 grms. of potassium iodide and diluting the ıtion to 100 c.c. Spots of this liquid are placed on a white tile and from time ime during the titration a little of the Fehling's solution in the flask is brought › contact with the indicator by means of a pointed glass rod. As long as educed copper is present blue iodide of starch will be formed. A more sitive indicator may be made by dissolving 1·5 grms. of ammonium thio-nate and 1 grm. of ferrous sulphate in 10 c.c. of water, adding 2·5 c.c. of centrated hydrochloric acid and decolorising the mixture with zinc dust.

The gravimetric method is more accurate. 25 c.c. of Fehling's solution are ted with an equal volume of distilled water in a beaker and heated on a water-ı at the boiling point until the liquid has attained the temperature of the er. A measured volume of the sugar solution is then added and sufficient ing water to bring the volume up to 100 c.c. The beaker is covered with a k glass and placed in the boiling water for twelve minutes. The precipitated rous oxide is filtered off through a weighed Gooch crucible, washed several

times with hot water, then with alcohol and ether. The oxide may be dried and weighed, or converted into cupric oxide by ignition. The oxide found is converted into sugar content by multiplying by the following factors:

Sugar.	Cu_2O.	CuO.
Dextrose, ... Levulose, ... Invert sugar, ...	0·5042	0·4535
Sucrose after inversion, . .	0·4536	0·4079
Starch and dextrin after hydrolysis,	0·4538	0·4081

A certain amount of auto-reduction takes place when Fehling's solution is heated alone. This should be determined when the solution is made up and allowed for; it does not amount to more than 0·002 grm. of CuO for 50 c.c. of the solution. It is important to remember that different results are obtained if the conditions of the reaction are varied, and that the weight of sugar taken for the test should give from 0·15 to 0·35 grm. of cuprous oxide. The cuprous oxide, after filtering and washing, may be determined by titration with decinormal potassium permanganate solution. The method of Knecht and Thompson (*J. Soc. Dyers and Col.*, 1920, 225) is simple: The asbestos mat and cuprous oxide are washed into a beaker containing about 2 grms. of iron alum dissoved in dilute sulphuric acid. The cuprous oxide reduces its equivalent of ferric sulphate and the ferrous sulphate produced is determined by titration with decinormal potassium permanganate solution. The reduction reaction is

$$Cu_2O + H_2SO_4 + Fe_2(SO_4)_3 = 2\,CuSO_4 + 2\,FeSO_4 + H_2O.$$

CHAPTER V.

ANALYSIS OF ORGANIC COMPOUNDS.

The Detection and Determination of Organic Nitrogen.

ITROGEN may be detected by means of the following tests: (1) A little the substance is mixed intimately with finely powdered soda-lime and the ixture heated in a hard glass test-tube. In the presence of nitrogen, ammonia given off, which may be recognised by its smell or its power of forming a black ain when a piece of filter paper moistened with mercurous nitrate solution is ld at the mouth of the tube. (2) A small piece of sodium is placed in a test-be, then a little of the substance to be tested, and finally another fragment of dium. The end of the tube is drawn out to prevent entrance of air. The tube then heated in a Bunsen flame, gently at first, and finally to a red heat. Any trogen present will be converted into sodium cyanide. The hot tube is dipped to cold water in a porcelain dish, or allowed to cool first and then broken into e dish. The solution is filtered and a little sodium hydroxide, ferric chloride d ferrous sulphate added, after which the mixture is heated for a few minutes d cooled. Upon acidifying the cold liquid with hydrochloric acid a precipitate coloration of Prussian blue is produced. Azo-compounds do not give this action. The formation of Prussian blue is represented by the equations

$$Fe(OH)_2 + 6\,NaCN = Na_4Fe(CN)_6 + 2\,NaOH,$$
$$Na_4Fe(CN)_6 + 2\,Fe_2(OH)_6 + 12\,HCl = Fe_4[Fe(CN)_6]_3 + 12\,NaCl + 12\,H_2O.$$

There are three methods for the determination of organic nitrogen, namely:

(1) Dumas' method.
(2) The method of Will and Varrentrap.
(3) The Kjeldahl method.

Dumas' Method.—This depends upon the fact that when organic substances heated with copper oxide, the nitrogen which they contain is given off as rogen gas or oxides of nitrogen, the carbon and hydrogen being oxidised carbon dioxide and water, respectively. The oxides of nitrogen, if present, decomposed by passing the products of combustion over more heated copper de, and after removing the water and carbon dioxide by means of potassium lroxide solution, the nitrogen is collected and measured. The volume of the ogen at N.T.P. is found, and the corresponding weight calculated.

Method of Will and Varrentrap.—The substance is mixed with finely powdered a-lime and heated in a combustion tube connected to an absorption apparatus taining a known volume of decinormal acid. The ammonia which is produced artly expelled from the tube during the combustion, the remainder being wn off by breaking the other end of the tube (which is drawn out to a fine it) and sucking air through the apparatus. The method is not much used is not so accurate as either the Dumas or Kjeldahl process.

Kjeldahl Method.—When organic compounds containing nitrogen (except azo-, nitro- and nitroso-compounds) are heated with concentrated sulphuric acid, they are completely decomposed and the nitrogen is changed into ammonium sulphate. This is decomposed by distilling with excess of sodium hydroxide. The ammonia which is liberated is received in a measured volume of standard hydrochloric or sulphuric acid and that portion of the acid unneutralised by the ammonia is determined by titration.

As much of the sample as will contain about 0·5 grm. of nitrogen is weighed out and transferred to a long-necked hard glass flask (*Durosil, Jena, Pyrex* or

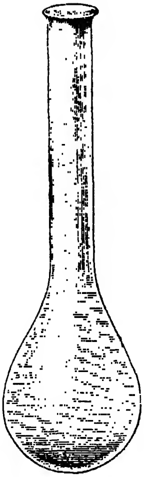


Fig. 25.—Kjeldahl Flask.

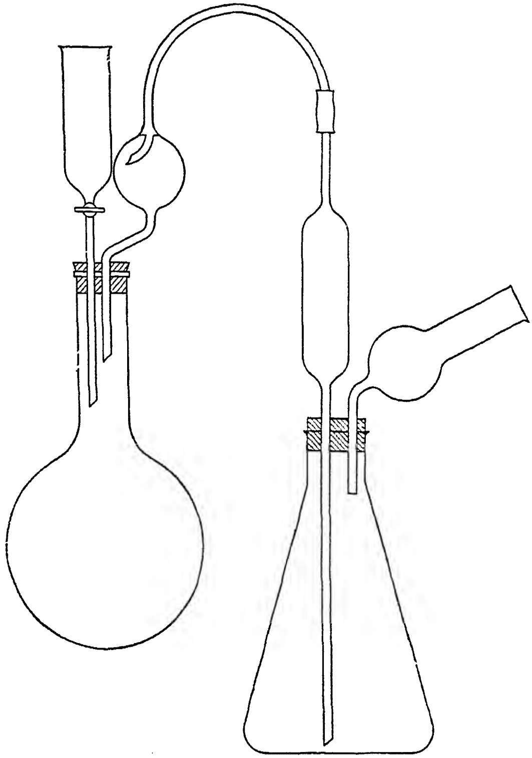


Fig. 26.—Kjeldahl Apparatus.

similar glass) (fig. 25). 20 c.c. of concentrated sulphuric acid are then run in and the sample thoroughly wetted by the acid. A small piece of copper foil or a crystal of copper sulphate is introduced and the flask supported on an asbestos sheet having a circular hole $1\frac{1}{2}$ inches in diameter in which the bottom of the flask is rested. The flask is inclined at an angle and the exposed base heated slowly by means of a direct flame, the operation being carried out in a fume-cupboard. The inclination of the flask prevents the ejection of drops of the reactants if bumping takes place. When all the organic matter has dissolved, about 5 grms. of ammonia-free potassium sulphate are added to the flask and the rate of heating is increased and heating continued until the liquid loses its brownish coloration. The heating is still continued for a further 15-30 minutes, or until the liquid is perfectly green (if iron is present in the sample the liquid will have a yellowish-

een appearance). On the conclusion of the foregoing process the contents of e flask are allowed to cool, washed into a 250-c.c. graduated flask and diluted the mark at 15·5° C. After well mixing and cooling, 50 c.c. of the resulting lution are pipetted into a round-bottomed flask, closed by a rubber bung rrying a tap-funnel and spray trap as shown in fig. 26.

An excess of concentrated sodium hydroxide solution over that required for mplete neutralisation of the acid present is introduced into the tap funnel. c.c. of decinormal sulphuric acid are then pipetted into a 500-c.c. conical sk connected to the spray trap by means of the bulbed tube illustrated, and a nch of powdered pumice added to the distillation flask to prevent bumping. ie capacity of the bulb of the bulb-tube should be sufficient to prevent any uid sucking back from the conical flask into the distillation flask. The end of e bulb-tube should reach below the level of the liquid in the conical flask. ie side-tube shown in the illustration may be connected to a U-tube ntaining sulphuric acid to prevent access of ammonia vapour from the atmo-here to the contents of the flask. When the apparatus is connected up as own, the sodium hydroxide is run in from the tap-funnel, care being taken leave a little in the funnel to act as a seal. When sufficient sodium droxide has been added a precipitate of cupric hydroxide will be formed. ie distillation is then commenced slowly and allowed to proceed until 100-150 :. of liquid have been collected in the conical flask, which is kept cool by immer-n in a water bath. In the case of liquids having a tendency to bump, it is tter to carry out the distillation with the aid of steam. On completion of the stillation the bulb-tube is disconnected from the spray-tap and the tap of the nnel removed altogether to avoid it becoming cemented by the action of the ong caustic alkali. The bung carrying the bulb-tube is then loosened and e tube washed down into the conical flask. The contents of the flask are then rated with tenth-normal sodium hydroxide, using cochineal as indicator, to termine the free acid remaining. The use of cochineal is preferred to methyl inge since the colour change of the latter is less readily detected, especially artificial light.

The calculation of the nitrogen present is made in the following manner :

$$(\text{c.c. } N/10\ H_2SO_4 - \text{c.c. } N/10\ \text{NaOH}) \times 0{\cdot}0014$$
$$= \text{grms. } N_2 \text{ in volume of liquid distilled (50 c.c.),}$$

$$(\text{c.c. } N/10\ H_2SO_4 - \text{c.c. } N/10\ \text{NaOH}) \times 0{\cdot}007$$
$$= \text{grms. } N_2 \text{ in weight of sample treated:}$$

In dealing with certain specific substances the following factors may be ployed :

Per cent. $N_2 \times 5{\cdot}62$ = per cent. hide substance or keratin.
,, $N_2 \times 5{\cdot}42$ = per cent. peptones.
,, $N_2 \times 6{\cdot}25$ = per cent. proteins.

Winkler (*J.S.C.I.*, 1913, 485) recommended distilling the ammonia into ic acid solution. It may then be titrated directly with decinormal hydro-oric acid, either methyl orange or congo red being used as indicator, neither ng sensitive to boric acid. For 0·1 to 0·29 grm. of ammonia, 5 grms. of boric l and 100 c.c. of water should be placed in the receiver. Scales and Harrison *ialyst*, 1920, 223) also recommended this method, but found that bromophenol e was the best indicator to use.

Kjeldahl Method for the Determination of Nitrogen in the Presence of Cyanides and Nitro-compounds.—In the presence of nitro-compounds and nitriles (cyanides) the accuracy of the method is affected (*vide supra*), and either of the following variations should be employed: (*a*) After transferring the weighed portion of the sample to the Kjeldahl flask and adding sulphuric acid, about 1 grm. of phenol is added, the flask kept cool and repeatedly shaken during about 10 minutes; 5 grms. of sodium thiosulphate and 10 grms. of potassium sulphate are then added and the digestion carried out as before. (*b*) The following method due to Jodlbauer (*Zeitsch. anal. Chem.*, **27**, 92) is recommended by Treadwell: The weighed sample is treated in a Kjeldahl flask with 20 c.c. of concentrated sulphuric acid and 2·5 c.c. of phenolsulphonic acid (prepared by dissolving 50 grms. of phenol in enough sulphuric acid of sp. gr. 1·04 to make 100 c.c. of solution); 2-3 grms. of zinc dust and 5 drops of chloroplatinic acid are added and the mixture digested for 4 hours over a direct flame. The liquid is then allowed to cool and distilled in the usual manner.

The Determination of Nitrogen in Dyestuffs.—When dyestuffs contain only amino- or substituted amino-groups, the ordinary Kjeldahl method may be used for the determination of the nitrogen. When azo- or nitro-groups are present, however, the modified process of Jodlbauer is necessary, since azo-compounds do not give correct results unless first reduced. Sisley and David (*Bull. Soc. Chim.*, 1929, **45**, 312) recommend the following process: The finely divided substance (0·5-1·0 grm.) is warmed with a mixture of 10 c.c. of alcohol and 5 c.c. of distilled water in a 250-c.c. *Pyrex* flask and 2-4 grms. of sodium hydrosulphite added in portions of 1 grm., the mixture being boiled and cooled after each addition. 10 c.c. of sulphuric acid are then added and the alcohol removed by heating. When the contents of the flask become pasty, 0·5 grm. of copper sulphate, 6-8 grms. of potassium sulphate (*i.e.*, 10 grms., less the amount of hydrosulphite) and 12 c.c. of sulphuric acid are added and the Kjeldahl process continued. Before distilling occurs, 5 c.c. of a freshly prepared 20 per cent. solution of sodium sulphide and a little granulated zinc are added, heating being continued for 45 minutes.

The Use of Oxygen Carriers.—Organic substances show considerable divergence in the ease with which they are oxidised by concentrated sulphuric acid. In order to facilitate oxidation "oxygen carriers" are always employed, together with "assistants" such as potassium sulphate, which raise the boiling-point of the mixture. Some discretion must be exercised in the use of these "oxygen carriers" and "assistants"; thus, if too much potassium sulphate be used, the boiling-point will be raised to a point at which loss of ammonia is occasioned by volatilisation of the ammonium sulphate. The amount of potassium sulphate employed should, roughly speaking, not exceed 5 grms. for each 20 c.c. of concentrated sulphuric acid used.

"Oxygen carriers," as their name suggests, greatly shorten the time required for oxidation by liberating free oxygen in their alternate oxidation and reduction. The most frequently used oxygen carriers are mercury, copper and copper sulphate. The use of mercury introduces an additional step in the process, since the element combines with part of the ammonia present to form mercurammines, which must be decomposed by the addition of ammonia-free sodium sulphide to the liquid before distillation, until the whole of the mercury is precipitated as sulphide. As a general rule it is preferable to use copper or copper sulphate. Some advantage is also obtained by using cupric compounds in the determination of protein nitrogen in that if the oxidation is not complete, a violet coloration (Biuret reaction) is produced on the addition of alkali prior to distillation.

Iany other bodies besides mercury and copper have been proposed as ygen carriers" or direct oxidisers. Sborowsky (*Ann. Chim. Analyt.*, 1922, 266) s that mercurous iodide makes the oxidation from five to ten times as l as when mercury itself is used. Among direct oxidising agents the following uitable, but they tend to cause some loss of nitrogen: potassium permante, potassium persulphate, potassium perchlorate and hydrogen peroxide; bodies are useful sometimes in the case of substances which are difficult ecompose, but they must be added very carefully and in small quantities. (*Collegium*, 1923, 93) found that the time necessary for complete decomion could be reduced to 20 minutes by using hydrogen peroxide.

'owerful oxidising agents must not be added at the beginning of the process, o the hot liquid during digestion; the contents of the digestion flask must llowed to cool first, and a little of the oxidising agent then added, *e.g.* 'stal of potassium permanganate or 5 c.c. of hydrogen peroxide solution, ontents of the flask then being warmed gently to promote oxidation.

'etermination of Nitrogen by Means of Formaldehyde.—The formation of methylene tetramine by the action of formaldehyde on ammonium sulphate een made the basis of a method for the determination of organic nitrogen ich the distillation stage of the Kjeldahl process is rendered unnecessary Hennet, *Coll.*, 1909, 197; Shaw, *Analyst*, 1924, 558). The reaction taking is in accordance with the equation

$$6\,HCHO + 2\,(NH_4)_2SO_4 = (CH_2)_6N_4 + 6\,H_2O + 2\,H_2SO_4,$$

the determination is carried out in the following manner: The digestion of veighed portion of the sample is carried out in the usual manner with conated sulphuric acid. On cooling, 50 c.c. of water are added and the liquid d to expel sulphur dioxide; a piece of red litmus paper is then added. bulb of the Kjeldahl flask is immersed in running water and a 40 per solution of sodium hydroxide cautiously added to a point at which the ion just remains acid. The liquid is again boiled to expel carbon dioxide duced by the sodium hydroxide, and on cooling is transferred to a 250-c.c. uated flask and made up to volume. 25 c.c. of the solution are pipetted into ation flask and 5 drops of a 1 per cent. solution of phenolphthalein added; ormal sodium hydroxide solution is then added until the liquid is alkaline. liquid is then just acidified with tenth-normal sulphuric acid and boiled ously to expel carbon dioxide, after which tenth-normal sodium hydroxide ded until the colour change from colourless to pink is just perceptible; ther drop of the sodium hydroxide solution is then added to produce a led pink coloration. This gives the "accurate" neutralisation point. '.—The sodium hydroxide solution employed in this neutralisation and in ubsequent titration must be of the same strength.) 5-10 c.c. of formaldeof predetermined acidity are then added from a pipette and the mixture ed to stand for a few minutes. The acid liberated is titrated with tenthal sodium hydroxide solution until the first appearance of a pink coloration ted, and 1-2 drops more alkali added to produce the decided pink colour sponding to "accurate" neutralisation. Correction is then made for cidity of the formaldehyde added and the amount of nitrogen in the 25 c.c. ution taken is calculated. The titration should be carried out in duplicate plicate and the mean of the results taken. To determine the acidity of the ldehyde used, 5 c.c. are diluted with 10-15 c.c. of freshly-boiled distilled and tenth-normal sodium hydroxide solution run in until the liquid is y neutral, when it is boiled for a short time to expel carbon dioxide. The

liquid is then cooled and the titration continued until a faint pink coloration is obtained; a further 1–2 drops of the standard alkali are then added to obtain a decided pink colour. The acidity of the formaldehyde, calculated from the sodium hydroxide used, is expressed as sulphuric acid, or the direct reading subtracted from the volume of sodium hydroxide used in the principal titration.

When only small quantities of the substance under investigation are available, 0·05 grm. of the sample is weighed out and transferred to a boiling tube with 7·5 c.c. of concentrated sulphuric acid and a small crystal of copper sulphate. The tube is then heated over a micro-burner. As soon as charring begins, 0·5 grm. of fused potassium bisulphate is added and the liquid heated until nearly colourless, then treated in the manner already described, except that after the approximate neutralisation and boiling, 0·02-normal sodium hydroxide is employed to adjust accurately to neutrality, and is also used in the subsequent titration.

Nessler Colorimetric Method.—When the sample contains very little nitrogen, or only a small quantity of the sample is available, the following colorimetric method may be employed (Ridge, *J.T.I.*, 1924, T 97). The solutions employed are prepared in the following way:—

Solution A.—75 grms. of potassium iodide are dissolved in 50 c.c. of warm water, 100 grms. of mercuric iodide added and the mixture stirred until solution is complete. The liquid is then diluted with about 400 c.c. of water, filtered and the filtrate made up to 1 litre.

Solution B.—This solution consists of a 10 per cent. solution of sodium hydroxide, free from carbonate.

For the preparation of the Nessler solution 200 c.c. of solution *B* are added to 300 c.c. of solution *A* and the mixture diluted to one litre.

A standard ammonia solution is also required and is prepared by dissolving 1·178 grms. of pure dry ammonium sulphate in one litre of water. Each cubic centimetre of this solution is equivalent to 0·25 milligramme of nitrogen.

The sample is digested with concentrated sulphuric acid and potassium bisulphate as described for the formaldehyde titration method for small quantities. The mixture is then distilled with alkali from a hard glass flask into a 50 c.c. measuring flask (fig. 27), sufficient water being placed in the latter to cover the end of the silica tube used, and 40 c.c. of distillate collected. This is mixed with 7·5 c.c. of the Nessler solution, made up to 50 c.c. and filtered after well shaking, the filtrate being collected in a Nessler cylinder. At the same time a number of standards are prepared to contain the amount of nitrogen expected in the weight of sample used, say by diluting 2·0, 2·5 and 3·0 c.c. of the standard solution respectively with 40 c.c. of water, adding 7·5 c.c. of Nessler solution to each and making up to volume (50 c.c.). After standing for 10 minutes the solutions of the sample and of the standards are compared with regard to colour by standing the cylinders on a white porcelain tile and looking down the axes of the cylinders. The nitrogen present in the sample is determined from the volume of the standard solution required to produce a coloration which exactly matches that obtained by "Nesslerising" the sample.

Ridge's Titrimetric Method.—This method of determining the nitrogen content of materials containing only small quantities of the element has been adopted by the Cotton Research Association (Ridge, *loc. cit.*). The weighed sample is covered with 6 c.c. of concentrated sulphuric acid in a hard glass boiling tube, 19 cms. long and 2·5 cms. diameter, 0·04 c.c. of mercury added and the tube closed with a pear-shaped glass bulb. The tube is then heated over a small flame until frothing ceases. 2 grms. of potassium bisulphate are added and the liquid gently boiled for about 3 hours, to obtain a clear,

colourless liquid, care being taken not to superheat the walls of the boiling tube. After a further short period of boiling (to ensure complete oxidation), the mixture is transferred to a hard glass distillation flask *A* (fig. 27), of 500 c.c. capacity, and diluted with ammonia-free distilled water to approximately 200 c.c. A few pieces of freshly-ignited broken earthenware are introduced into the distilling flask and the head-piece and delivery tube *C D E F* attached. The end of the delivery tube is inserted beneath the surface of an accurately-measured volume (2–2·5 c.c.) of *N*/10 hydrochloric acid contained in the titration vessel *C* (fig. 28). Sufficient 40 per cent. sodium hydroxide solution (30-40 c.c.) is added from the funnel *B* to render the contents of the flask alkaline, and finally 2 c.c. of a saturated solution of sodium sulphide are also added. The

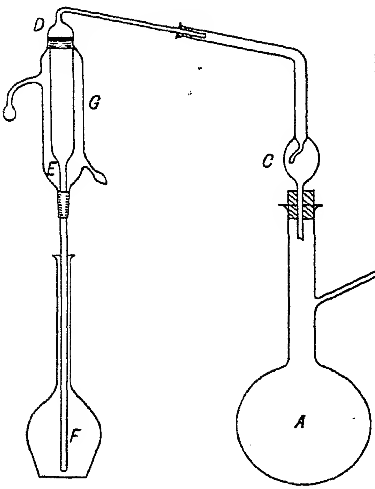


Fig. 27.—Ridge's Apparatus.

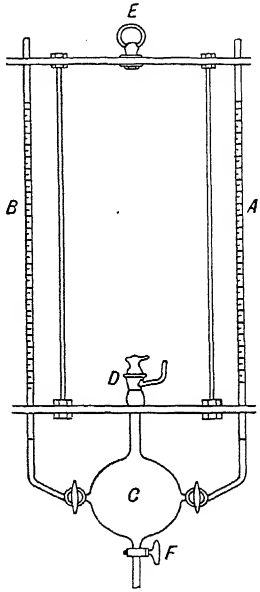


Fig. 28.—Ridge's Titration Apparatus.

ammonia is then distilled over at a rate such that 50 c.c. of distillate are present after about 30 minutes. The distilling apparatus is then removed, after washing the end of the tube, and the remaining excess of acid titrated with *N*/10 sodium hydroxide free from carbonate, using methyl red as indicator. To correct the results for the small quantities of ammonia invariably contained in the reagents and carried over during the distillation, blank experiments to determine this ammonia should frequently be carried out. For this purpose 6 c.c. of the sulphuric acid, 0·04 c.c. of the mercury and 2 grms. of the potassium bisulphate are digested for 3 hours and the mixture then made alkaline with the sodium hydroxide solution, 2 c.c. of the sodium sulphide solution added, the whole then being distilled and titrated as already described. The average correction is about 0·03 c.c. on the total titration of about 2 c.c.

The titration apparatus, fig. 28, consists of two burettes *A* and *B*, of 3 c.c.

total capacity, graduated to 0·01 c.c. These contain standard acid and alkali respectively and are permanently sealed to the titration bulb *C* in such a way that either solution can be directly admitted to the titrated liquid. The capacity of the bulb is about 150 c.c. and it is closed with a hollow ground stopper through which connection to the atmosphere can be made when necessary, the whole apparatus being supported in a light framework on the neck *D* of the titration bulb. The framework is suspended by the swivel ring *E*, which enables the apparatus to be shaken during titration. The washing-out of the bulb is effected by means of the outflow tube and tap *F*. The burettes can be read accurately to 0·002 c.c.; they must be carefully standardised and kept scrupulously free from grease. The form and quality of the head-piece and delivery tube *C D E F* in the distillation apparatus are of importance, both extraction of alkali from the glass and mechanical transfer of minute traces of alkali during distillation being sources of serious error. Ridge, from whose paper the foregoing description is taken, uses a glass head-piece *C* attached by means of a cork to the silica delivery tube.

The Determination of Chlorine.

Chlorine (bromine or iodine) is detected by the following test: A little of the substance is heated with metallic sodium in the same way as for the detection of nitrogen; the fused mass is extracted with water and the extract filtered. If the substance contained chlorine, this element will be present in the filtrate as sodium chloride. The filtrate is acidified with dilute nitric acid, treated with excess of silver nitrate solution and boiled to coagulate the precipitate, which is then filtered off. Many organic substances contain nitrogen as well as chlorine, and in this case the precipitate will contain silver cyanide. To eliminate this the precipitate is collected and dried, then heated gently in a porcelain crucible until it fuses. This decomposes silver cyanide with the formation of metallic silver, whilst silver chloride is not affected. The fused mass is digested with dilute nitric acid, which dissolves the metallic silver, leaving the silver chloride undissolved.

There are two standard methods for the determination of chlorine in organic compounds, viz.:

(1) The Carius method.
(2) The lime method.

The Carius Method.—This depends upon the fact that when an organic compound is heated with nitric acid under pressure in the presence of silver nitrate, the chlorine which it contains is converted quantitatively into silver chloride, which may be filtered off and weighed. Sulphur, phosphorus and arsenic are oxidised simultaneously to sulphuric, phosphoric and arsenic acids, respectively.

A tube of resistance-glass, about 50 cms. in length and 2 cms. in diameter, is sealed off at one end, cleaned and dried. From 0·5 to 1 grm. of silver nitrate is introduced into the tube and about 40 c.c. of chlorine-free nitric acid added by means of a long thistle funnel, so that the sides of the tube above the level of the acid are not wetted. The substance to be tested is weighed out (from 0·1 to 0·2 grm.) and placed in a small tube about 5 cm. in length and 5 mm. in width. The tube containing the nitric acid is inclined and the small tube is allowed to slide down until it reaches the acid, in which it will float when the weight of acid displaced is equal to that of the tube and its contents. The open

end of the tube is now heated carefully in a blow-pipe flame until the glass has become soft and begins to thicken; it is then drawn out into a thick walled capillary and sealed off. It is very important that the walls of the drawn-off end are thick, in order that they may be able to withstand pressure. When cold, the tube is wrapped in asbestos and placed in a furnace. The temperature of the furnace is raised very slowly during three hours to about 200° C., then during the next three hours to 250° C., and finally during a third three hours to 300° C. The tube is then allowed to cool and removed from the furnace. If any liquid is present in the capillary, this is driven back into the tube by means of a Bunsen flame. The tube is wrapped in a cloth and the capillary heated strongly until the glass becomes soft and the gases in the tube blow a hole through it and escape. When no more gas escapes, the capillary is scratched with a file and touched with a hot glass rod to break it off. The contents of the tube are then poured into a beaker, both the tube and capillary being well rinsed out into the beaker with water. The contents of the beaker are diluted to about 300 c.c. and boiled to coagulate the silver chloride. This is then filtered off through a weighed Gooch crucible, washed, dried at 130° C. and weighed. ($AgCl \times 0{\cdot}24736 = Cl$).

The Lime Method.—In this method, which is in some respects simpler in operation than that due to Carius, the substance is ignited with pure lime, which converts chlorine into calcium chloride. This is dissolved and precipitated with silver nitrate, the silver chloride being then filtered off and weighed. The lime used obviously must be perfectly free from chlorine, and should contain no sulphates. A combustion tube is sealed off at one end, and pure lime is introduced to a depth of about 5 cms. On top of this is placed the weighed quantity of the substance to be tested, then more lime (about 5 cms.), the substance and lime being mixed by means of a copper wire ending in a small spiral. The tube is then nearly filled with lime, laid on its side and tapped until a free space is left above the surface of its contents. It is then placed in a combustion furnace and the open end heated to dull redness. After this the other end is heated similarly, and then the whole tube is brought gradually to a dull red heat. The tube is then cooled and its contents transferred to a beaker containing an excess of dilute nitric acid. Any insoluble carbon is filtered off, and the chlorine in the filtrate is precipitated with silver nitrate in the usual manner. When compounds containing much nitrogen are treated in this way some calcium cyanide is formed, which will also be precipitated by the silver nitrate. In this case the method of Nebauer and Kerner should be used: The cyanide and chloride are precipitated together by adding excess of silver nitrate solution at room temperature, the precipitate filtered off, dried and weighed. A weighed quantity of the mixed precipitate is placed in a porcelain crucible, a drop of nitric acid added and the crucible heated until the precipitate begins to fuse. The fused mass is covered with dilute sulphuric acid, a piece of pure zinc is added and the crucible allowed to stand for some hours. The mixture is then filtered and the chlorine determined in the filtrate by means of silver nitrate.

Method of Piria and Schiff.—This method is very suitable for such substances as chlorinated wool, or any other substance which is not very volatile. From 0·1 to 0·3 grm. of the substance is placed in a small platinum crucible which is then filled completely with a mixture of anhydrous sodium carbonate (1 part) and calcium oxide (4 parts). The crucible is then placed in a larger one, its open top resting on the bottom, and the outer crucible is filled with the mixture of sodium carbonate and calcium oxide until the inverted crucible is covered. The outer crucible is heated over a large Bunsen flame, or by a

blow-pipe, in such a manner that the outer portions of the mixture become heated highly before the contents of the smaller crucible, after which the temperature of the whole is brought to dull redness. After cooling, the mass is extracted with water, acidified with dilute nitric acid, filtered if necessary, and the chlorine precipitated with silver nitrate.

The Determination of Sulphur.

Sulphur may be detected in organic compounds by the following reactions :—

(1) A little of the substance is mixed with sodium peroxide in an iron crucible, and the mixture covered with a layer of the peroxide. The crucible is then heated very carefully. In many cases it is sufficient to touch the mixture with a heated copper wire. When oxidation is complete, the residue is dissolved in water, the solution acidified with hydrochloric acid and tested for sulphate by means of barium chloride.

(2) The substance is heated with metallic sodium, as in the nitrogen test. The filtrate from the aqueous extract will contain sodium sulphide. This may be detected by adding a little freshly prepared solution of sodium nitroprusside, when a violet colour will be produced. Or, if a little of the solution be placed on a silver coin, a black stain of silver sulphide will result.

Sulphur is determined by the *Carius method*, already described, except that no silver nitrate is used. The solution, after oxidation, is diluted, precipitated with barium chloride at the boiling-point, and the barium sulphate filtered off and weighed. ($BaSO_4 \times 0{\cdot}13737 = S$).

In the case of textile fibres or protein derivatives, the *Benedict-Denis method* is reliable and much simpler in operation. It is described under the analysis of wool.

Phosphorus.

When an organic substance containing phosphorus is heated with sodium peroxide, the phosphorus is oxidised to sodium phosphate. If the solution of the fused mass be acidified with nitric acid and warmed with a solution of ammonium molybdate, a yellow precipitate of ammonium phosphomolybdate will be formed.

Phosphorus is determined quantitatively either by the Carius method or by igniting the substance with a mixture of potassium carbonate and a little potassium nitrate ; in the first case phosphoric acid is produced and in the second potassium phosphate. The phosphoric acid is precipitated with magnesia mixture or ammonium molybdate in the usual manner.

The method of Neumann (*Analyst*, 1909, 507), as modified by Plimmer and Bayliss, is especially suitable for proteins such as wool: About 0·2 grm. is placed in a Kjeldahl flask and 10 c.c. of sulphuric acid and 10 c.c. of nitric acid are added. The contents of the flask are then heated until colourless, just as in the Kjeldahl method, except that a little nitric acid is added from time to time. The liquid is cooled and diluted with 150 c.c. of water, then 100 c.c. of a 50 per cent. solution of ammonium nitrate added. The solution is then warmed, a slight excess of a 10 per cent. solution of ammonium molybdate added, and the whole shaken for a minute and then allowed to stand for a short time, after which the precipitate is filtered off on a Gooch crucible and washed with a little cold water. The precipitate and asbestos are then washed back into the flask, and semi-normal sodium hydroxide solution added from a burette until the precipitate has dissolved, and then a further 5 c.c. are run in. The contents of

the flask are boiled to expel the ammonia which is formed by decomposition of the sodium ammonium phosphate, the liquid cooled, diluted to 150 c.c. and a little phenolphthalein added. If the phenolphthalein does not become pink, more sodium hydroxide is added and the solution boiled again. Semi-normal sulphuric acid is then run in from a burette, about 1 c.c. above the volume required to discharge the pink colour being added. The liquid is then boiled to expel carbon dioxide and titrated back with semi-normal sodium hydroxide. Each c.c. of $N/2$ sodium hydroxide solution corresponds to 0·0005536 grm. of phosphorus.

Arsenic.

The detection and determination of arsenic are often of importance in dealing with textile products. For both qualitative and quantitative tests it is essential that the organic matter should be first destroyed. This may be accomplished by the Carius method, by heating with sodium peroxide or with a mixture of potassium carbonate and potassium nitrate. A simpler and equally effective method is to ignite the substance with magnesia, or with magnesia containing a little magnesium nitrate. When much arsenic is present, it may be precipitated either as trisulphide, As_2S_3, or as magnesium ammonium arsenate, $MgNH_4AsO_4$, but the latter method is only available when phosphates are absent.

In the sulphide method the ignited mass is dissolved in dilute hydrochloric acid and the solution filtered. The filtrate is treated with a little potassium metabisulphite (free from arsenic) and boiled until free from sulphur dioxide. The solution is then cooled, made strongly acid with hydrochloric acid and saturated with sulphuretted hydrogen. The precipitated arsenic trisulphide is filtered into a weighed Gooch crucible, washed with hot water, dried at 105° C. and weighed. ($As_2S_3 \times 0{\cdot}60906 = As$).

In the second method, the solution is treated by the method of Levol (Treadwell, *Analytical Chemistry*, Vol. II., p. 206). It should not contain more than 0·1 grm. arsenic per 100 c.c., and is treated, with constant stirring and drop by drop, with 5 c.c. of concentrated hydrochloric acid. For each 0·1 grm. of arsenic are added 7-10 c.c. of magnesia mixture and a drop of phenolphthalein solution. Next, 10 per cent. ammonia solution is added from a burette, with stirring, until a pink colour is produced, and then sufficient of the ammonia solution to make one-third of the total liquid. The mixture is allowed to stand for 12 hours and then filtered through a weighed Gooch crucible. The precipitate is washed with 2·5 per cent. ammonia solution and finally once with a saturated solution of ammonium nitrate made alkaline with ammonia. The crucible and contents are then ignited, at first gently, and finally strongly, to convert the magnesium ammonium arsenate into magnesium pyroarsenate, $Mg_2As_2O_7$, then cooled and weighed. ($Mg_2As_2O_7 \times 0{\cdot}48272 = As$).

Arsenic may be identified in organic matter by the *Reinsch test*. The sample is mixed with hydrochloric acid and a small piece of clean copper foil is suspended in the liquid, which is heated gently on a water-bath. When arsenic is present it is deposited on the copper, forming a steely deposit. The copper is washed with water, alcohol and ether, and dried. It is then placed in an ignition tube and heated gently. The arsenic is oxidised to arsenious oxide, which volatilises and forms a characteristic crystalline deposit on the upper cool portion of the tube. The crystals are identified by microscopic examination.

Colorimetric Determination of Arsenic.—When only small quantities of arsenic are present, either the Marsh or Gutzeit test is employed. Both of these depend upon the fact that arsenious compounds are converted into arseniuretted

hydrogen by nascent hydrogen. In the *Marsh test* the arseniuretted hydrogen, together with the excess of hydrogen, is passed through a capillary tube, which is heated at a particular point. The arseniuretted hydrogen is decomposed at this point and the arsenic is deposited in the form of a mirror, which is compared with mirrors made from known quantities of arsenious oxide. In the *Gutzeit test* the arseniuretted hydrogen is passed through a small circle of filter paper which has been treated with a solution of mercuric chloride, and the resulting yellow coloration is compared with a set of standards made in a similar way. The hydrogen for both tests may be generated from zinc and acid or by electrolysis. The latter method has advantages, since it dispenses with the use of zinc, which may itself contain arsenic. Electrolytic hydrogen is used commonly for the Marsh test, but zinc and hydrochloric acid are generally employed for the Gutzeit method.

The Gutzeit Test (*British Pharmacopoeia*, 1914).—The apparatus used consists of a wide-mouthed bottle of about 120 c.c. capacity, fitted with a rubber bung through which passes a soft glass tube about 20 cm. in length, having an internal diameter of 5 mm. and an external diameter of 7 mm. The upper end is widened to a bore of 8 mm., the lower end drawn out to a bore of about 1 mm., and a small hole of about 2 mm. diameter is blown in the side of the tube where it is constricted.

The following reagents are required :—

(1) Lead papers, consisting of pieces of thin white filter-paper (100 mm. × 40 mm.) soaked in a solution of lead acetate and dried.

(2) Mercuric chloride papers, made by soaking smooth white filter-paper in a saturated aqueous solution of mercuric chloride, drying, and cutting into circles of 5·5 cm. diameter. These are kept in a stoppered bottle in a dark cupboard.

(3) Hydrochloric acid, sulphuric acid and zinc, all of which must be of the purity known as " As T."

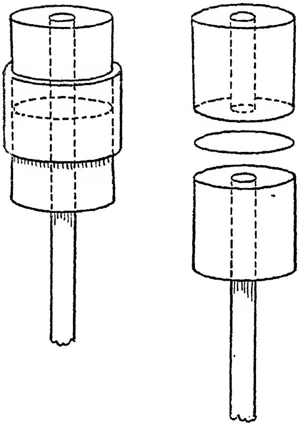
(4) " Stannated " hydrochloric acid, made by diluting 1 c.c. of stannous chloride solution (" As T ") to 100 c.c. with hydrochloric acid. The stannous chloride solution is prepared from the B.P. stannous chloride solution by adding an equal volume of hydrochloric acid, concentrating to the original bulk and filtering. B.P. stannous chloride solution is made by diluting 60 c.c. of hydrochloric acid with 20 c.c. of distilled water, adding 20 grms. of tin and warming the mixture gently until gas is no longer given off. Sufficient water is then added to produce 100 c.c. of solution, allowing the undissolved tin to remain in the liquid.

(5) A solution of arsenious oxide, containing 0·00001 grm. per c.c. ; this must be prepared freshly before use by diluting a stronger standard solution.

The test is carried out in the following manner :—A strip of the lead paper is rolled up and placed in the glass tube so that the upper end is not less than 2 cm. below the top of the tube. A piece of the mercuric chloride paper is now placed over the top of the tube and secured by a rubber ring. The tube is inserted in the rubber bung. The acidified solution to be examined is placed in the bottle and 10 grms. of zinc (" As T ") added. The rubber bung with the glass tube attached is placed quickly in position so that the lower end is clear of the surface of the liquid and the hole in the constricted portion of the tube is below the bottom of the bung. The action should be allowed to proceed for 30 to 40 minutes, the mercuric chloride paper not being exposed to strong sunlight. The action may be accelerated by standing the apparatus on a hot plate, care being taken that the mercuric chloride paper remains quite dry throughout the test. The stains fade on keeping, and those used for comparison

should be freshly prepared. Much trouble is saved by using a series of painted stains which, if kept in the dark, can be used for a long time.

It is desirable, when two stains have to be compared, that both should be of the same shape and also sharp in outline. The method of fixing the paper disc by means of a rubber band does not fulfil these conditions. Stubbs (*Analyst*, 1927, 699) recommends the following method, which ensures that all the evolved gas passes through that portion of the paper only which covers the end of the glass tube. Two corks, each about 1 inch in diameter, are bored centrally to the external diameter of the glass tube. This tube, which is unflanged, and has its end ground flat, is inserted in one cork so as to be just flush with its upper surface. A glass collar, about $\frac{3}{4}$ inch long, is made from glass tubing of about



Figs. 29 and 30.—Fixing Mercuric Chloride Paper Disc.

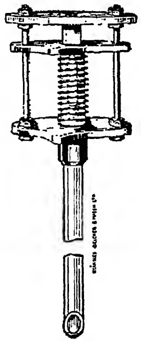


Fig. 31.—Fixing $HgCl_2$ Paper—Wilkie's Method.

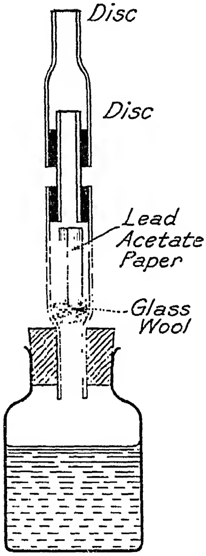


Fig. 32.—Cribb's Apparatus.

1 inch internal diameter. Into this collar the cork bearing the glass tube is fitted from below, and the other from above. When both corks are pressed home they should meet at about the middle of the collar. A disc of mercuric chloride paper is placed on the surface of the lower cork before inserting the upper one. By this means the paper is held firmly against the ground end of the glass tube, ensuring stains of sharp outline, and thus facilitating comparisons. Fig. 29 shows the arrangement fitted up ready for use, and fig. 30 shows the two corks separated and the disc of mercuric chloride paper between them.

Another way of fixing the disc, due to Wilkie, is seen in fig. 31. It employs a metal cylinder to the top of which is fixed a metal plate. The cylinder is cemented to the tube so that the plate is about 10 mm. from the top. A movable plate, provided with a cylindrical base, is connected with a bakelite plate by two metal rods which pass through holes in the fixed plate. The bakelite

plate is held in position at the top of the tube by a spring and can be moved upwards to allow insertion of the mercuric chloride paper by holding the fixed plate and pressing the movable plate towards it. The bakelite plate is provided with a hole of the same diameter as the internal diameter of the glass tube and

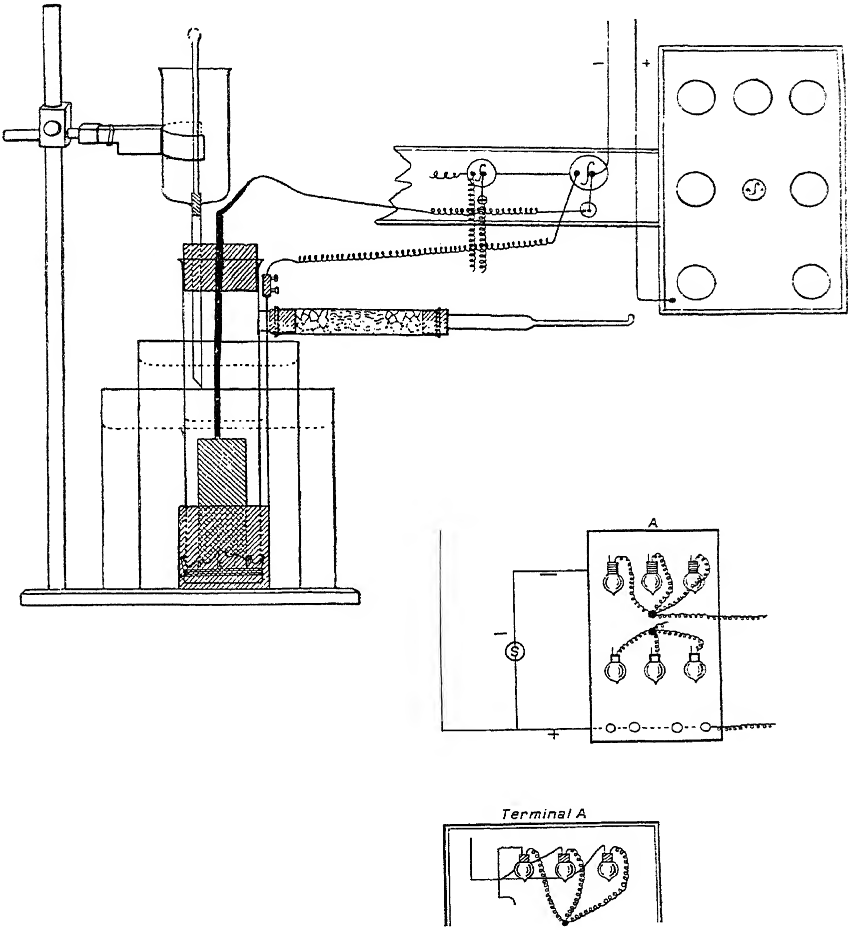


Fig. 33.—Electrolytic Arsenic Apparatus.

slightly counter-sunk on the lower side. The tube, which has a hole about 2 mm. in diameter about 10 mm. from the bottom, may be fitted by means of a bung into a suitable bottle.

The apparatus illustrated in fig. 32 is due to Cribb (*Analyst*, 1927, 701). Small discs of mercuric chloride paper of standard size are cut with a cork borer

and uniformly and securely gummed to the upper ground ends of the two thick-walled glass tubes, so that all the gas evolved must pass through the discs. The tubing employed has an external diameter of not less than 11 mm. and a bore of 5 mm.

As a general rule it is necessary to destroy organic matter before testing for arsenic, and also to reduce the arsenic to the arsenious state.

Organic matter can be destroyed by mixing the substance with excess of arsenic-free magnesia and incinerating. The addition of a little magnesium nitrate is made sometimes to assist oxidation. When moist oxidation is preferable, nitric acid may be used. After destruction of the organic matter the solution must be treated with a reducing agent. For this purpose the solution of stannous chloride described may be employed, or potassium metabisulphite, the liquid subsequently being boiled until free from sulphurous acid. The arsenic may be separated from the other matter by distillation with hydrochloric acid, and this procedure is sometimes adopted.

Electrolytic Method.—A simple form of electrolytic apparatus (Trotman, *J.S.C.I.*, 1904, 177) is illustrated in fig. 33. It consists of a double electrolytic cell, the inner chamber being connected to a delivery tube carrying a drying tube and a drawn-out hard glass tube for the deposition of the arsenic. The drying tube is filled with cotton wool, previously soaked in lead acetate solution and dried, and calcium chloride. The lower end of the inner cell is covered with parchment paper and the upper end is fitted with a rubber bung through which pass an electrode forming the cathode, consisting of arsenic-free lead, and a tap funnel. The inner cell is surrounded by a circular lead electrode which serves as the anode. The current is obtained from the mains supply by passage through a rheostat which may be made of lamps arranged so that they are in parallel with each other but in series with the cells. Sufficient lamps must be used to give a current of about 5 ampères. Dilute (10 per cent.) sulphuric acid is placed in the outer cell and sufficient in the inner cell to cover the lower portion of the electrode. The current is then passed through the apparatus until the air has been expelled. A small Bunsen flame is then placed beneath the delivery tube at the point where the capillary commences and the current passed through for a further ten minutes. If at the end of this time no mirror has been produced, the apparatus may be regarded as being free from arsenic. The solution to be tested for arsenic is now introduced through the tap funnel, and if there is any tendency to frothing, a few drops of amyl alcohol may be added. The passage of the current is continued for 20 minutes. The mirror obtained is compared with a set of standards made in a similar manner with a standard solution of arsenious oxide. The standards should commence with 0·000001 grm. of the oxide. The material to be tested is burnt with magnesia and reduced in the manner described above.

A good electrolytic apparatus due to Monier-Williams is illustrated in fig. 34, in which the cathode consists of lead foil wrapped round a glass rod and the anode of a piece of lead foil surrounding the inner cell which consists of a porous pot.

The Determination of Arsenic in Dyestuffs.—The following method has been recommended by a sub-committee appointed to investigate the various methods used (*Analyst*, 1930, 102): The organic matter is destroyed by a process of wet oxidation by means of nitric acid; the arsenic is then separated by distillation with hydrochloric acid and the distillate is tested by a modified Gutzeit test.

Approximately accurate results may be obtained by a direct distillation

method, except in the case of certain dyestuffs such as nigrosine. The method is useful for sorting out. It is carried out as follows : Five grams of the dyestuff are weighed into a 100 c.c. Kjeldahl flask of resistance glass or silica, with a

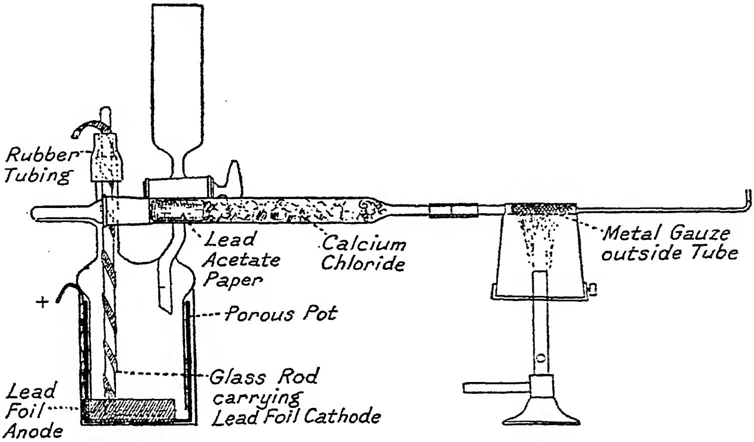


Fig. 34.—Monier-Williams Apparatus.

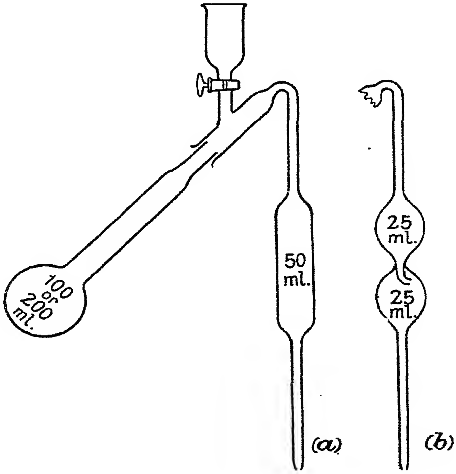


Fig. 35.—Distillation Apparatus for Arsenic in Dyestuffs.
Length of Flask Neck, 7″ to 8″.
Length of Condenser, 18″ to 20″.

ground-in condenser, into which has been blown a tap funnel, as shown in fig. 35*a*. A mixture of 20 c.c. of concentrated sulphuric acid and 14 c.c. of water,

previously cooled to 5° C., is then added to the colour in the flask, and the whole is thoroughly mixed, the mixture meanwhile being cooled externally. While still cooling, 5 grms. of a mixture made up in the following proportions—5 grms. sodium chloride, 0·5 grm. hydrazine sulphate, 0·02 grm. potassium bromide—are added, followed rapidly by 10 c.c. of concentrated hydrochloric acid. Care should be taken that no solid material comes in contact with the ground-in portion of the flask. The mixture of chloride-hydrazine-bromide can be made up in bulk, and will keep indefinitely in a tightly stoppered bottle.

The condenser is quickly fitted and the mixture distilled into 10 c.c. of water and 2 c.c. of nitric acid (sp. gr. 1·42) contained in a receiver which is cooled externally. (If difficulty due to frothing is experienced, 2 c.c. of amyl alcohol may be added to the contents of the Kjeldahl flask at the commencement of the distillation, in which case the "end point" is taken as that point at which amyl alcohol appears in the condenser and the bulb of the condenser is full of vapour). The exit end should dip below the surface of the liquid. When all or nearly all of the hydrochloric acid has distilled over (indicated by the appearance of steam in the condenser, accompanied by a strong tendency to suck back), the distillation is stopped, and the receiver changed. The contents of the Kjeldahl flask are then cooled to room temperature, a further quantity of 10 c.c. of concentrated hydrochloric acid is added slowly, through the tap funnel in the condenser, and the distillation continued into a further quantity of 10 c.c. water and 2 c.c. nitric acid (sp. gr. 1·42) until the hydrochloric acid has again been driven off. The first and second distillates are mixed and evaporated to dryness on the water-bath in a porcelain basin.

5 c.c. of water are then added and evaporated to dryness, and this is repeated to make sure that all the nitric acid has been eliminated. The residue is then dissolved by warming with 3 c.c. of concentrated sulphuric acid, the liquid cooled and cautiously diluted to 25 c.c. with water. The solution is then ready for transference to the arsenic apparatus, described later.

The following method, whilst more tedious than the direct distillation method, must be used to obtain accurate results: Five grams of the sample are treated with 10 c.c. of 30 per cent. nitric acid in a 100 c.c. or 200 c.c. resistance glass or silica Kjeldahl flask, or in the distillation flask already referred to. (If excessive frothing is experienced in the early stages, the preliminary treatment may be carried out in a 500 c.c. beaker until frothing has been brought well under control. The mixture is then transferred to the Kjeldahl flask, the subsequent procedure being as above.) The mixture, after any initial vigorous reaction has subsided, is heated until any further vigorous action ceases, then cooled, and 10 c.c. of concentrated sulphuric acid gradually added at such a rate as not to cause excessive frothing or heating (10 minutes is usually required), and the heating is continued until the liquid appreciably darkens in colour. To the hot solution 5 c.c. of nitric acid (1·42 sp. gr.) are added slowly, in small portions, and the liquid boiled down until colourless or pale yellow. If this amount of nitric acid is insufficient to bring about the desired decolorisation, further acid is added in small portions at a time, preferably by dropping in from a burette, note being kept of the amount. After cooling, the liquid is diluted with 50 c.c. of water and transferred to the flask of the special distillation apparatus shown in fig. 35, or to a similar apparatus without the tap funnel. The solution is first boiled down, without inserting the condensing arm, to 10 c.c., or until white fumes appear, cooled, diluted, and again boiled down to 10 c.c., cooled and 7 c.c. of water added. The liquid is well cooled and 5 grms. of the chloride-hydrazine-bromide mixture referred to in the direct distillation

method are introduced through a short-stemmed funnel (avoiding contamination of the ground portion of the neck of the flask), followed immediately by 10 c.c. of concentrated hydrochloric acid. The condenser is fitted quickly and the liquid distilled into an externally-cooled mixture of 10 c.c. of water and 2 c.c. of nitric acid until its volume is reduced by about one half, or until about 5 minutes after the condenser is full of steam, the exit end of the condenser dipping beneath the surface of the liquid. The distillate is made up directly to 25 c.c. with water and a suitable aliquot portion taken for transference to the apparatus subsequently described. The distillate is then evaporated to dryness on the water-bath, the residue twice evaporated to dryness with 5 c.c. of water to remove nitric acid, dissolved by warming in 3 c.c. of concentrated sulphuric acid and diluted to 25 c.c. with water, as described under the direct distillation method.

If the form of condenser shown in fig. 35*a* does not effectively prevent sucking back, the type shown in fig. 35*b* may be substituted. The process may be shortened appreciably by distilling into 10 c.c. of saturated bromine water instead of into dilute nitric acid. In this case care must be taken that there is an excess of bromine water in the receiver at the end of the distillation. No attempt should be made to boil off the excess of bromine from the distillate or loss of arsenic may ensue.

Certain colours, particularly basic dyestuffs, give trouble in the oxidation process, owing to their liability to violent deflagration. In such cases the following modification of the previous method may be employed: Five grams of the dyestuff are placed in a resistance glass or silica Kjeldahl flask and 25-30 c.c. of 30 per cent. nitric acid are added. The mixture is warmed until the initial vigorous reaction is over. At this point the formation of a spongy or tarry cake is usually observed. The mixture is cooled and the acid liquor poured off. The tarry material in the flask is washed with the smallest possible quantity of water, and the washings added to the acid liquor. To the tarry residue are added 10 c.c. of concentrated sulphuric acid and the contents of the flask agitated until the residue is dispersed. Concentrated nitric acid is then added drop by drop until vigorous oxidation is over, the mixture being warmed if necessary. The poured-off acid liquor is returned to the flask and the mixture is boiled down until the colour just commences to darken. Destruction is completed as in the previous method. (If it is found that the tarry matter cannot be satisfactorily treated in the Kjeldahl flask, it may be transferred to a 600 c.c. beaker. In this case it may be necessary to use rather more than 10 c.c. of sulphuric acid for the subsequent treatment. If more than 10 c.c. of acid are used, the solution is boiled down to the corresponding volume and water in the proportion already described, that is 7 c.c. of water for each 10 c.c. of acid, is added.)

The Determination of Arsenic in the Prepared Solution.—The arsenic in the prepared solution from the direct distillation process, or from the distillation process following the oxidation process, is determined by the following method: The apparatus for carrying out the test should be exactly as defined in the British Pharmacopoeia, 1914, with the following exception:—The gas exit tube should have an internal diameter of 4 mm. and should not be widened out at the gas exit end, but should be ground smooth at right angles to the tube. The test papers are prepared by soaking smooth-surfaced filter paper, similar in substance and texture to No. 1 Whatman filter paper, in a saturated aqueous solution of mercuric chloride, and are dried in a warm atmosphere without exposure to bright daylight. The edges of the dry papers are rejected and the

papers must be kept in the dark until required. The mercuric chloride paper should be used in the test in the form of a disc held flatly and firmly against the ground end of the tube by any suitable means. The method recommended by the British Pharmacopoeia, 1914, in which the test paper is secured at the end of the tube by means of a rubber band, is not a satisfactory method ; more effective methods are those which have already been described (*Analyst*, 1927, 700).

In carrying out the test, either the whole of the solution (corresponding to 5 grms. of dyestuff) or, if the arsenic content is more than 1 part per million, such an aliquot portion as will contain from 0·004 to 0·010 mgrm. As_2O_3 is mixed with sulphuric acid, stannated hydrochloric acid and water, in the following proportions :—

x c.c. of prepared distillate,
$25 - x$ c.c. of 1·8 sp. gr. sulphuric acid,
8 c.c. of stannated hydrochloric acid B.P.,
and water to make up to 60 c.c.

The mixture is transferred to the apparatus, 10 grms. of granulated zinc are added, and the apparatus immediately assembled. It is essential that the zinc used shall not only be free from arsenic, but that it shall also be " active." A blank determination should give no stain on the test paper under the conditions of the test, but should give a definite stain when 0·001 mgrm. of As_2O_3 is present.

The reaction is allowed to proceed without the application of external heat for 15 minutes, the mercuric chloride paper being protected from strong light; the reaction vessel is then transferred to a water-bath maintained at 35-40° C. for 30 minutes. The stain produced on the paper is compared with a series of freshly made standard stains prepared by using a known amount of As_2O_3 in tests carried out under the conditions as standardised in the foregoing, a suitable range being 0·001 to 0·010 mgrm., the stains being examined under normal daylight conditions. Adequate precautions are to be taken and blank tests made to ensure that the apparatus and all reagents used give no visible stain.

The Identification and Determination of Mineral Constituents.

In the case of a simple organic compound, such as the salt of an acid, the mineral constituents may be identified without destroying the organic matter. But when the compound is complex in nature, such as a dyestuff, it is necessary to remove the organic matter before commencing the analysis.

About 5 grms. of the substance are burnt to an ash in a platinum or silica dish and the weight of the ash is determined. It is important to remember that alkali metals are partially volatilised at high temperatures, and that mercury, arsenic, antimony and zinc, may also be lost ; these must be looked for separately.

When none of these metals is present, the substance may be ashed in a muffle and the ash examined in the ordinary manner. A useful way of destroying organic matter when volatile metals are likely to be present is to heat the substance with concentrated sulphuric acid in a Kjeldahl flask until a colourless solution is obtained. A little hydrogen peroxide or a little perchloric acid may be added from time to time to assist oxidation. When oxidation is complete, the solution is cooled, diluted with water and allowed to stand for some time. Any lead sulphate which may have been precipitated is filtered off and the filtrate is treated in the usual manner. When no other metals have

been detected, the ash may be regarded as consisting of sodium or potassium, although if it has been heated strongly, both of these may have been volatilised. When attention must be directed specially towards the detection or determination of sodium and potassium, the following procedure should be adopted: A weighed quantity of the substance should be charred carefully so that it will give a colourless filtrate when extracted. The charred mass is boiled with dilute hydrochloric acid and filtered. The residue on the filter is washed with water, then incinerated and again extracted with dilute hydrochloric acid. The combined extracts and washings are heated to the boiling point and treated with small quantities of barium hydroxide until the mixture has an alkaline reaction to litmus paper. The liquid and precipitate are washed into a graduated flask, cooled, diluted to the mark with water and filtered. An aliquot part of the filtrate is taken and treated, at the boiling point, with solid ammonium carbonate and a little ammonium oxalate. The precipitate is filtered off and washed with carbon dioxide-free water. The filtrate is evaporated to dryness and ignited at a low temperature until free from ammonium salts. The residue is then dissolved in dilute hydrochloric acid, filtered if necessary, evaporated, dried in an oven and weighed. This residue consists of the chlorides of the alkali metals present. Potassium is separated in the following manner: The residue is dissolved in a little water, the solution placed in a small porcelain dish, and a little 20 per cent. solution of perchloric acid added. The liquid is evaporated on a hot plate until it begins to fume. The residue is then cooled, redissolved in a little water, a few more drops of perchloric acid added, again evaporating and cooling. A little alcohol is now added and the mixture filtered through a weighed Gooch crucible. The dish is washed out with a saturated alcoholic solution of potassium perchlorate and the precipitate on the filter is washed also with the same solution. The crucible is then dried and weighed ($KClO_4 \times 0{\cdot}33996 = K_2O$).

Sodium may be detected by the method of Feldstein and Ward (*Analyst*, 1931, 245), in which nickel uranyl acetate is used. A mixture of 70 grms. of uranium acetate, 60 c.c. of glacial acetic acid and 940 c.c. of water is warmed and stirred until the salt is dissolved. The solution is allowed to stand at room temperature for several hours with occasional stirring, and then filtered through a dry filter into a dry bottle. When 2 c.c. of the reagent are added to a 0·1 per cent. solution of sodium chloride a light green precipitate is obtained. With a 2 per cent. solution of potassium chloride no immediate precipitate is formed, but a slight precipitate settles after a few hours.

CHAPTER VI.

ACIDS.

Hydrochloric Acid.

The chief impurities in commercial hydrochloric acid are sulphuric acid and sulphates, sodium chloride, iron, chlorine and nitric acid. The detection and determination of these are described in the following.

The amount of hydrochloric acid present in a commercial sample may be determined approximately from the specific gravity. The relation between specific gravity and concentration of hydrochloric acid solutions is given in the table opposite.

The accurate determination of the hydrochloric acid present is effected by titration with a standard decinormal solution of silver nitrate. The total acidity of the sample is determined by titration with decinormal alkali.

Sulphuric Acid, Sulphates and Chlorides.—The presence of sulphuric acid or sulphates is indicated if a white precipitate is formed on adding a 10 per cent. solution of barium chloride to a diluted portion of the sample. For the quantitative estimation of sulphuric acid, sulphates and chlorides the following method is employed:

A weighed quantity of the sample is transferred to a porcelain basin and evaporated as far as possible on a water-bath. The residue is diluted with water and the mixture again evaporated to expel the last traces of the volatile hydrochloric acid and any free chlorine or nitric acid which may be present. The residue is now again diluted with water and titrated with a decinormal solution of sodium hydroxide, the acidity being expressed in terms of sulphuric acid.

To determine sulphates and chlorides present, a weighed quantity of the acid is transferred to a silica evaporating basin and carefully evaporated to dryness and the residue ignited at a low temperature for a short period. The residue is then dissolved in a little water, the solution transferred to a graduated flask and the volume made up. A portion of this solution is pipetted into a titration flask and the chlorides present are determined by titration with a tenth-normal solution of silver nitrate, using potassium chromate as indicator. 1 c.c. of the silver nitrate solution is equivalent to 0·00585 grm. of sodium chloride. Another portion of the solution is pipetted into a beaker, acidified with hydrochloric acid and boiled. While still boiling a 10 per cent. solution of barium chloride is added and any precipitated barium sulphate is filtered off, ignited and weighed. If chlorides are absent the sulphate residue obtained by evaporation may be regarded as sodium sulphate.

Iron is detected by diluting the sample with water and adding a solution of potassium ferrocyanide.

Free *chlorine*, if present, will liberate iodine from potassium iodide.

Nitric acid may be detected by the brown ring test or by means of diphenylamine.

Specific Gravity of Hydrochloric Acid.

°Bé.	Sp. Gr.	°Tw.	% HCl.	°Bé.	Sp. Gr.	°Tw.	% HCl.	°Bé.	Sp. Gr.	°Tw.	% HCl.
1·00	1·0069	1·38	1·40	16·0	1·1240	24·80	24·57	20·8	1·1675	33·50	32·93
2·00	1·0140	2·80	2·82	16·1	1·1248	24·96	24·73	20·9	1·1684	33·68	33·12
3·00	1·0211	4·22	4·25	16·2	1·1256	25·12	24·90	21·0	1·1694	33·88	33·31
4·00	1·0284	5·68	5·69	16·3	1·1265	25·30	25·06	21·1	1·1703	34·06	33·50
5·00	1·0357	7·14	7·15	16·4	1·1274	25·48	25·23	21·2	1·1713	34·26	33·69
5·25	1·0375	7·50	7·52	16·5	1·1283	25·66	25·39	21·3	1·1722	34·44	33·88
5·50	1·0394	7·88	7·89	16·6	1·1292	25·84	25·56	21·4	1·1732	34·64	34·07
5·75	1·0413	8·26	8·26	16·7	1·1301	26·02	25·72	21·5	1·7441	34·82	34·26
6·00	1·0432	8·64	8·64	16·8	1·1310	26·20	25·89	21·6	1·1751	35·02	34·45
6·25	1·0450	9·00	9·02	16·9	1·1319	26·38	26·05	21·7	1·1760	35·20	34·64
6·50	1·0469	9·38	9·40	17·0	1·1328	26·56	26·22	21·8	1·1770	35·40	34·83
6·75	1·0488	9·76	9·78	17·1	1·1336	26·72	26·39	21·9	1·1779	35·58	35·02
7·00	1·0507	10·14	10·17	17·2	1·1345	26·90	26·56	22·0	1·1789	35·78	35·21
7·25	1·0526	10·52	10·55	17·3	1·1354	27·08	26·73	22·1	1·1798	35·96	35·40
7·50	1·0545	10·90	10·94	17·4	1·1363	27·26	26·90	22·2	1·1808	36·16	35·59
7·75	1·0564	11·28	11·32	17·5	1·1372	27·44	27·07	22·3	1·1817	36·34	35·78
8·00	1·0584	11·68	11·71	17·6	1·1381	27·62	27·24	22·4	1·1827	36·54	35·97
8·25	1·0603	12·06	12·09	17·7	1·1390	27·80	27·41	22·5	1·1836	36·72	36·16
8·50	1·0623	12·46	12·48	17·8	1·1399	27·98	27·58	22·6	1·1846	36·92	36·35
8·75	1·0642	12·84	12·87	17·9	1·1408	28·16	27·75	22·7	1·1856	37·12	36·54
9·00	1·0662	13·24	13·26	18·0	1·1417	28·34	27·92	22·8	1·1866	37·32	36·73
9·25	1·0681	13·62	13·65	18·1	1·1426	28·52	28·09	22·9	1·1875	37·50	36·93
9·50	1·0701	14·02	14·04	18·2	1·1435	28·70	28·26	23·0	1·1885	37·70	37·14
9·75	1·0721	14·42	14·43	18·3	1·1444	28·88	28·44	23·1	1·1895	37·90	37·36
10·00	1·0741	14·82	14·83	18·4	1·1453	29·06	28·61	23·2	1·1904	38·08	37·58
10·25	1·0761	15·22	15·22	18·5	1·1462	29·24	28·78	23·3	1·1914	38·28	37·80
10·50	1·0781	15·62	15·62	18·6	1·1471	29·42	28·95	23·4	1·1924	38·48	38·03
10·75	1·0801	16·02	16·01	18·7	1·1480	29·60	29·13	23·5	1·1934	38·68	38·26
11·00	1·0821	16·42	16·41	18·8	1·1489	29·78	29·30	23·6	1·1944	38·88	38·49
11·25	1·0841	16·82	16·81	18·9	1·1498	29·96	29·48	23·7	1·1953	39·06	38·72
11·50	1·0861	17·22	17·21	19·0	1·1508	30·16	29·65	23·8	1·1963	39·26	38·95
11·75	1·0881	17·62	17·61	19·1	1·1517	30·34	29·83	23·9	1·1973	39·46	39·18
12·00	1·0902	18·04	18·01	19·2	1·1526	30·52	30·00	24·0	1·1983	39·66	39·41
12·25	1·0922	18·44	18·41	19·3	1·1535	30·70	30·18	24·1	1·1993	39·86	39·64
12·50	1·0943	18·86	18·82	19·4	1·1544	30·88	30·35	24·2	1·2003	40·06	39·86
12·75	1·0964	19·28	19·22	19·5	1·1554	31·08	30·53	24·3	1·2013	40·26	40·09
13·00	1·0985	19·70	19·63	19·6	1·1563	31·26	30·71	24·4	1·2023	40·46	40·32
13·25	1·1006	20·12	20·04	19·7	1·1571	31·44	30·90	24·5	1·2033	40·66	40·55
13·50	1·1027	20·54	20·45	19·8	1·1581	31·62	31·08	24·6	1·2043	40·86	40·78
13·75	1·1048	20·96	20·86	19·9	1·1590	31·80	31·27	24·7	1·2053	41·06	41·01
14·00	1·1069	21·38	21·27	20·0	1·1600	32·00	31·45	24·8	1·2063	41·26	41·24
14·25	1·1090	21·80	21·68	20·1	1·1609	32·18	31·64	24·9	1·2073	41·46	41·48
14·50	1·1111	22·22	22·09	20·2	1·1619	32·38	31·82	25·0	1·2083	41·66	41·72
14·75	1·1132	22·64	22·50	20·3	1·1628	32·56	32·01	25·1	1·2093	41·86	41·99
15·00	1·1154	23·08	22·92	20·4	1·1637	32·74	32·19	25·2	1·2103	42·06	42·30
15·25	1·1176	23·52	23·33	20·5	1·1647	32·94	32·38	25·3	1·2114	42·28	42·64
15·50	1·1197	23·94	23·75	20·6	1·1656	33·12	32·56	25·4	1·2124	42·48	43·01
15·75	1·1219	24·38	24·16	20·7	1·1666	33·32	32·75	25·5	1·2134	42·68	43·40

ALLOWANCE FOR TEMPERATURE.

10°–15° Bé. — 1/40° Bé. or 0·0002 sp. gr. for 1° F.

15°–22° Bé. — 1/30° Bé. or 0·0003 „ „ 1° F.

22°–25° Bé. — 1/28° Bé. or 0·00035 „ „ 1° F.

Sulphuric Acid.

The impurities present in technical sulphuric acid vary considerably according to the method of manufacture. They include nitric acid, nitrous acid, lead and iron.

The specific gravity of the sample is determined and the approximate percentage of pure sulphuric acid ascertained by reference to the following table :

SPECIFIC GRAVITY OF SULPHURIC ACID.

° Bé.	Sp. Gr.	° Tw.	Per cent. H_2SO_4.	° Bé.	Sp. Gr.	° Tw.	Per cent. H_2SO_4.
0	1·0000	0·0	0·00	37	1·3426	68·5	43·99
1	1·0069	1·4	1·02	38	1·3551	71·0	45·35
2	1·0140	2·8	2·08	39	1·3679	73·6	46·72
3	1·0211	4·2	3·13	40	1·3810	76·2	48·10
4	1·0284	5·7	4·21	41	1·3942	78·8	49·47
5	1·0357	7·1	5·28	42	1·4078	81·6	50·87
6	1·0432	8·6	6·37	43	1·4216	84·3	52·26
7	1·0507	10·1	7·45	44	1·4356	87·1	53·66
8	1·0584	11·7	8·55	45	1·4500	90·0	55·07
9	1·0662	13·2	9·66	46	1·4646	92·9	56·48
10	1·0741	14·8	10·77	47	1·4796	95·9	57·90
11	1·0821	16·4	11·89	48	1·4948	99·0	59·32
12	1·0902	18·0	13·01	49	1·5104	102·1	60·75
13	1·0985	19·7	14·13	50	1·5263	105·3	62·18
14	1·1069	21·4	15·25	51	1·5426	108·5	63·66
15	1·1154	23·1	16·38	52	1·5591	111·8	65·13
16	1·1240	24·8	17·53	53	1·5761	115·2	66·63
17	1·1328	26·6	18·71	54	1·5934	118·7	68·13
18	1·1417	28·3	19·89	55	1·6111	122·2	69·65
19	1·1508	30·2	21·07	56	1·6292	125·8	71·17
20	1·1600	32·0	22·25	57	1·6477	129·5	72·75
21	1·1694	33·9	23·43	58	1·6667	133·3	74·36
22	1·1789	35·8	24·61	59	1·6860	137·2	75·99
23	1·1885	37·7	25·81	60	1·7059	141·2	77·67
24	1·1983	39·7	27·03	61	1·7262	145·2	79·43
25	1·2083	41·7	28·28	62	1·7470	149·4	81·30
26	1·2185	43·7	29·53	63	1·7683	153·7	83·34
27	1·2288	45·8	30·79	64	1·7901	158·0	85·66
28	1·2393	47·9	32·05	64¼	1·7957	159·1	86·33
29	1·2500	50·0	33·33	64½	1·8012	160·2	87·04
30	1·2609	52·2	34·63	64¾	1·8068	161·4	87·81
31	1·2719	54·4	35·93	65	1·8125	162·5	88·65
32	1·2832	56·6	37·26	65¼	1·8182	163·6	89·55
33	1·2946	58·9	38·58	65½	1·8239	164·8	90·60
34	1·3063	61·3	39·92	65¾	1·8297	165·9	91·80
35	1·3182	63·6	41·27	66	1·8354	167·1	93·19
36	1·3303	66·1	42·63				

ALLOWANCE FOR TEMPERATURE.

At 10° Bé.	0·039° Bé.	or	0·00023	sp. gr.	=	1°	F.
,, 20°	,, 0·036°	,,	0·00034	,,	=	1°	,,
,, 30°	,, 0·035°	,,	0·00039	,,	=	1°	,,
,, 40°	,, 0·031°	,,	0·00041	,,	=	1°	,,
,, 50°	,, 0·028°	,,	0·00045	,,	=	1°	,,
,, 60°	,, 0·026°	,,	0·00053	,,	=	1°	,,
,, 63°	,, 0·026°	,,	0·00057	,,	=	1°	,,
,, 66°	,, 0·0235°	,,	0·00064	,,	=	1°	,,

A more accurate analysis may be carried out in the following manner:

A weighed quantity of the acid (16-20 grms.) is transferred to a litre flask containing distilled water, the mixture cooled and diluted to the mark with distilled water.

Total Acidity.—A portion of the diluted sample is pipetted into a titration flask and the total acidity determined by titration with decinormal sodium hydroxide solution in the presence of methyl orange. This gives the total acidity (*a*).

Nitrous acid (*b*) is calculated from the volume of decinormal potassium permanganate solution consumed, and the *total nitrogen* (*c*) is determined by the nitrometer method. The difference between (*b*) and (*c*) gives the *nitric acid*, whilst (*a*) less (*b*) + (*c*) gives the *sulphuric acid*.

Lead.—The presence of lead will be indicated by the formation of a turbidity or precipitate when the weighed sample is diluted with water. If present the diluted acid should be allowed to stand for some hours before analysis, the portions required being pipetted from the clear supernatant liquid. The lead may be determined in the original solution or a fresh portion may be weighed and diluted until it contains about 1 per cent. of acid. After standing for about 12 hours the liquid is filtered through a weighed silica Gooch crucible, the lead sulphate washed with 1 per cent. sulphuric acid, ignited gently until free from sulphuric acid and weighed. The precipitation of the lead is assisted by the addition of alcohol to the diluted acid.

Iron.—The filtrate from the foregoing determination is tested for iron by evaporating the solution to dryness and examining the residue in the manner described for the detection of iron in hydrochloric acid.

Nitric Acid.

The *acidity* is determined by titration. *Sulphates, sulphuric acid, chlorides* and *hydrochloric acid* are detected and determined in the usual manner. The table on page 84 gives the specific gravity of various concentrations of the acid in water.

Formic Acid, HCOOH.

Pure formic acid has a specific gravity of 1·241 at 0° C. It solidifies when cooled to a temperature below 8° C. and boils at 101° C. Commercial formic acid is a 50 to 90 per cent. solution of the acid in water. It is rarely adulterated, but may contain mineral acid or acetic acid.

Qualitative Tests for Formic Acid.—Silver formate is precipitated as colourless crystals when silver nitrate solution is added to a neutral concentrated solution of formic acid or a formate. The precipitate becomes dark on standing, and when warmed is reduced to metallic silver, either as a black precipitate or a mirror. When a formate is warmed in a test-tube with concentrated sulphuric acid, carbon monoxide is given off, which may be ignited at the mouth of the tube. When formic acid is heated with mercuric chloride solution a white precipitate of mercurous chloride or a black precipitate of metallic mercury is formed. Acetates do not give this reaction. When formates are warmed with alcohol and sulphuric acid, ethyl formate is given off, which has the smell of rum. Neutral solutions of formates give, like acetates, a red coloration with neutral ferric chloride, and when the solution is boiled a reddish precipitate of basic iron formate is produced.

Analysis of Formic Acid.—Formic acid is rarely adulterated, but it may contain mineral acids, acetic acid and iron. In the absence of other acids,

Specific Gravity of Nitric Acid.

The numbers marked * are the results of direct observations; the others are obtained by interpolation.

HNO_3, per cent.	Specific Gravity.		HNO_3, per cent.	Specific Gravity.		HNO_3, per cent.	Specific Gravity.	
	At 0° C.	At 15° C.		At 0° C.	At 15° C.		At 0° C.	At 15° C.
100·00	1·559	1·530	72·39*	1·455*	1·432*	45·00	1·300	1·284
99·84*	1·559*	1·530*	71·24*	1·450*	1·429*	43·53*	1·291*	1·274*
99·72*	1·558*	1·530*	69·96	1·444	1·423	42·00	1·280	1·264
99·52*	1·557*	1·529*	69·20*	1·441*	1·419*	41·00	1·274	1·257
97·89*	1·551*	1·523*	68·00	1·435	1·414	40·00	1·267	1·251
97·00	1·548	1·520	67·00	1·430	1·410	39·00	1·260	1·244
96·00	1·544	1·516	66·00	1·425	1·405	37·95*	1·253*	1·237*
95·27*	1·542*	1·514*	65·07*	1·420*	1·400*	36·00	1·240	1·225
94·00	1·537	1·509	64·00	1·415	1·395	35·00	1·234	1·218
93·01*	1·533*	1·506*	63·59	1·413	1·393	33·86*	1·226*	1·211*
92·00	1·529	1·503	62·00	1·404	1·386	32·00	1·214	1·198
91·00	1·526	1·499	61·21*	1·400*	1·381*	31·00	1·207	1·192
90·00	1·522	1·495	60·00	1·393	1·374	30·00	1·200	1·185
89·56*	1·521*	1·494*	59·59*	1·391*	1·372*	29·00	1·194	1·179
88·00	1·514	1·488	58·88	1·387	1·368	28·00*	1·187*	1·172*
87·45*	1·513*	1·486*	58·00	1·382	1·363	27·00	1·180	1·166
86·17*	1·507*	1·482*	57·00	1·376	1·358	25·71*	1·171*	1·157*
85·00	1·503	1·478	56·10*	1·371*	1·353*	23·00	1·153	1·138
84·00	1·499	1·474	55·00	1·365	1·346	20·00	1·132	1·120
83·00	1·495	1·470	54·00	1·359	1·341	17·47*	1·115*	1·105*
82·00	1·492	1·467	53·81	1·358	1·339	15·00	1·099	1·089
80·96*	1·488*	1·463*	53·00	1·353	1·335	13·00	1·085	1·077
80·00	1·484	1·460	52·33*	1·349*	1·331*	11·41*	1·075	1·067*
79·00	1·481	1·456	50·99*	1·341*	1·323*	7·22*	1·050	1·045*
77·66	1·476	1·451	49·97	1·334	1·317	4·00	1·026	1·022
76·00	1·469	1·445	49·00	1·328	1·312	2·00	1·013	1·010
75·00	1·465	1·442	48·00	1·321	1·304	0·00	1·000	0·999
74·01*	1·462*	1·438*	47·18*	1·315*	1·298*			
73·00	1·457	1·435	46·64	1·312	1·295			

formic acid is determined by titration with decinormal sodium hydroxide solution in the presence of phenolphthalein (factor = 0·0046).

Formic acid may be determined also by oxidising it by means of a standard solution of potassium permanganate in the presence of sulphuric acid. The reaction is represented by the equation

$$5\,HCOOH + 2\,KMnO_4 + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,CO_2.$$

The formic acid is diluted, mixed with a slight excess of sulphuric acid, and decinormal permanganate solution is run into the mixture at a temperature of about 60° C. until a permanent faint pink colour is produced. Each cubic centimetre of $N/10$ permanganate solution will oxidise 0·0046 grm. of formic acid.

The Determination of Formic Acid in the Presence of Acetic Acid.—Both formic acid and acetic acid react with freshly precipitated yellow mercuric oxide, but whilst mercuric formate is reduced to metallic mercury by boiling, mercuric acetate remains unchanged. The total acidity is first determined by titration. A measured volume of the acid is then boiled with an excess of

mercuric chloride solution, the mixture filtered and the precipitate washed with water. The filtrate will contain mercuric acetate if acetic acid was present; this is precipitated as mercuric sulphide by sulphuretted hydrogen, the sulphide filtered through a weighed Gooch crucible, washed, dried at 100° C. and weighed. From the weight of the precipitate, the equivalent of the acetic acid present is calculated. In the presence of formic acid, the residue of mercuric oxide will contain metallic mercury. The former is dissolved by digestion with dilute hydrochloric acid, the insoluble mercury being filtered off and weighed, giving the equivalent of the formic acid present.

Holmberg and Lindberg (*J.L.T.C.*, 1924, 313) recommend the following process depending on the reaction

$$HCOONa + 2\,HgCl_2 = NaCl + CO_2 + Hg_2Cl_2 + HCl.$$

The solution is neutralised, a measured excess of standard alkali and about a 50 per cent. excess of a solution of mercuric chloride added, and the mixture boiled gently under a reflux condenser for an hour. The solution is then acidified with a known volume of standard hydrochloric acid, a small quantity of a soluble bromide added and carbon dioxide expelled by boiling for half an hour. The solution is then cooled and titrated with standard alkali. The formic acid originally present is given by the sum of the two quantities of alkali added after the first neutralisation, less the volume of acid added. Acetic acid does not give this reaction.

Lead formate is only slightly soluble in water and insoluble in alcohol. Lead acetate is soluble in both alcohol and water. Hence acetic acid and formic acid may be separated by treating their solution with excess of lead carbonate, filtering, evaporating the filtrate to a small volume and adding a considerable volume of alcohol. The lead formate is filtered off, washed with alcohol, and weighed, whilst the lead acetate will be found in the filtrate.

Acetic Acid, CH_3COOH.

Qualitative Tests.—When acetic acid is warmed with alcohol and sulphuric acid, ethyl acetate is produced, which can be recognised by its smell. If the acid is neutralised with potassium hydroxide, evaporated to dryness and heated with an equal weight of arsenious oxide, the characteristic odour of cacodyl oxide is observed, but it should be noted that the compound is highly poisonous:

$$2\,As_2O_3 + 8\,CH_3COOH + 8\,KOH = 2\,As_2(CH_3)_4O + 4\,K_2CO_3 + 4\,CO_2 + 8\,H_2O.$$

Ferric chloride, when added to a neutral solution of an acetate, gives a red colour owing to the formation of ferric acetate. When the solution is boiled, a reddish precipitate of basic ferric acetate is formed and acetic acid is given off:

$$Fe_2(CH_3COO)_6 + 4\,H_2O = Fe_2(CH_3COO)_2\,(OH)_4 + 4\,CH_3COOH.$$

With concentrated neutral solutions of acetates, silver nitrate gives a white precipitate of silver acetate, but it is not reduced by boiling as in the case of silver formate.

The Determination of Acetic Acid.—Acetic acid containing water, corresponding to the formula $C_2H_4O_2 \cdot H_2O$, has a greater specific gravity than the anhydrous acid; hence the strength of a concentrated solution of acetic acid cannot be determined by means of its specific gravity, although

the method may be used for dilute solutions. The following table is given by Allen (*Commercial Organic Analysis, Vol. I.*) :

$C_2H_4O_2$ per cent.	Specific Gravity.		$C_2H_4O_2$ per cent.	Specific Gravity.	
	Oudemanns.	Mohr.		Oudemanns.	Mohr.
1	1·0007	1·001	21	1·0298	1·029
2	1·0022	1·002	22	1·0310	1·031
3	1·0037	1·004	23	1·0324	1·032
4	1·0052	1·005	24	1·0337	1·033
5	1·0067	1·007	25	1·0350	1·034
6	1·0085	1·008	26	1·0363	1·035
7	1·0098	1·010	27	1·0375	1·036
8	1·0113	1·012	28	1·0388	1·038
9	1·0127	1·013	29	1·0400	1·039
10	1·0142	1·015	30	1·0412	1·040
11	1·0157	1·016	31	1·0424	1·041
12	1·0171	1·017	32	1·0436	1·042
13	1·0185	1·018	33	1·0447	1·044
14	1·0200	1·020	40	1·0523	1·051
15	1·0214	1·022	50	1·0615	1·061
16	1·0228	1·023	60	1·0685	1·067
17	1·0242	1·024	70	1·0733	1·070
18	1·0256	1·025	80	1·0748	1·0735
19	1·0270	1·026	90	1·0713	1·0730
20	1·0284	1·027	100	1·0553	1·0635

It will be seen that according to Oudemanns the specific gravities for concentrations of 100 per cent. and about 43 per cent. acid are the same. Acetic acid may be determined like other organic acids by titration with standard sodium hydroxide solution using phenolphthalein as indicator.

Acetic acid may be determined also by adding an excess of pure barium carbonate, boiling the mixture and filtering. The dissolved barium in the filtrate is then determined by precipitation with sulphuric acid. 233 parts of barium sulphate are equivalent to 120 parts of acetic acid.

The separation of acetic acid from non-volatile acids may be effected by distillation, but several distillations are necessary. After distilling nearly to dryness the contents of the distilling flask are cooled, water is added and the liquid again distilled, the process being repeated until the distillate is free from the acid. The united distillates are then titrated with standard alkali. When hydrochloric acid is present some silver sulphate should be added to the liquid before distillation.

Glacial acetic acid should contain not less than 97 per cent. of pure acid, corresponding to a solidifying point of 11·95° C. *Water* may be detected by the following test : A little of the sample is mixed with dry carbon tetrachloride and a trace of iodine added. Anhydrous acetic acid dissolves completely, but if water is present, two layers are formed, the aqueous layer being coloured reddish-brown.

Commercial Acetic Acid.—The chief impurities in the commercial acid are sulphuric acid, sulphurous acid, hydrochloric acid, formic acid, sulphates, chlorides, lead, copper and iron. These may be detected by the usual qualitative reactions. *Sulphuric acid* and *sulphates* may be separated by evaporating some of the acid on a water-bath and adding 4 or 5 volumes of 95 per cent. alcohol. The sulphates remain undissolved, but the sulphuric acid passes into

solution. *Sulphurous acid* may be determined by the following method: An excess of barium chloride solution is added to the diluted acid and any precipitate which is formed is filtered off. Some bromine is added to the filtrate, which is then boiled to expel the excess. Any barium sulphate which is now precipitated will be due to sulphurous acid. This precipitate is filtered off and weighed. Its weight multiplied by 0·27446 gives sulphur dioxide.

Formic acid is present sometimes in acetic acid. Its determination has already been described, but the modification of Delahaye's method (*Analyst*, 1910, 488) should be referred to. *Lead*, *copper* and *iron* are determined by the colorimetric methods described in Chapter . Pyroligneous acid may contain *organic matter*. This may be estimated in the absence of formic acid or sulphurous acid by noting the volume of decinormal permanganate solution which is required to produce a permanent pink colour.

Oxalic Acid, COOH . COOH.

This acid crystallises with two molecules of water and the commercial acid corresponds to the formula $C_2H_2O_4 . 2\,H_2O$. Anhydrous oxalic acid sublimes without charring when heated. It dissolves readily in water or boiling alcohol. It is only slightly soluble in ether and insoluble in benzene, petroleum ether or chloroform. Commercial oxalic acid is, as a rule, a pure substance, but impurities such as oxalates, sulphates and sulphuric acid may sometimes be present.

Qualitative Reactions.—When oxalic acid is heated with concentrated sulphuric acid, a mixture of carbon monoxide and carbon dioxide is produced, but no charring occurs. If the test be carried out in a small flask fitted with a delivery tube, the gas may be passed through a test-tube containing barium hydroxide, which precipitates the carbon dioxide, and the carbon monoxide may then be ignited. When a warm solution of oxalic acid containing sulphuric acid is treated with potassium permanganate solution, the latter is decolorised so long as any excess of oxalic acid remains, and carbon dioxide is evolved:

$$COOH . COOH + O = 2\,CO_2 + H_2O.$$

An insoluble precipitate of calcium oxalate is formed when a solution of calcium chloride or calcium acetate is added to a solution of a neutral oxalate. The precipitate is insoluble in acetic acid but dissolves readily in mineral acids. Solutions of neutral oxalates give a precipitate of mercurous oxalate when treated with mercurous nitrate.

Determination of Oxalic Acid.—Oxalic acid may be determined by titration with decinormal sodium hydroxide in the presence of phenolphthalein (1 c.c. $N/10$ NaOH $\equiv$ 0·0045 grm. $C_2H_2O_4$ or 0·0063 grm. $C_2H_2O_4 . 2\,H_2O$). A better method is to titrate with decinormal potassium permanganate solution, but the solution must not contain other bodies which are capable of being oxidised. The solution to be titrated must be warm and a considerable excess of sulphuric acid must be present. The decinormal potassium permanganate solution is run in from a burette, with constant stirring, until a permanent pink colour is produced (1 cc. $N/10$ $KMnO_4 \equiv$ 0·0045 grm. $C_2H_2O_4$).

Oxalic acid is determined also as calcium oxalate. The solution is made alkaline with ammonia, heated to the boiling point and a slight excess of calcium chloride solution added to the boiling liquid. The precipitate is filtered off on a Gooch crucible and after washing, the asbestos mat and precipitate are rinsed into a beaker, treated with warm sulphuric acid, and the liberated oxalic acid titrated with decinormal potassium permanganate solution. The precipitate

may also be dried at 100° C. and weighed, or ignited to calcium oxide, but titration with potassium permanganate is quite accurate and more convenient. If sulphates are present, calcium sulphate should be used instead of calcium chloride as the precipitant; the use of calcium acetate has some advantages, since it avoids the precipitation of other calcium salts. Calcium oxalate is insoluble in acetic acid, whereas most of the other calcium salts are soluble; hence the precipitate may be purified if desired by digestion with cold dilute acetic acid.

Impurities are tested for in the usual manner. It may be noted that if the sample gives an ash which gives off carbon dioxide when treated with an acid, an acid oxalate is present.

Tartaric Acid, CHOH . COOH . CHOH . COOH.

Commercial tartaric acid may contain traces of iron, lead or copper, and salts of calcium, but high-grade samples contain nearly 100 per cent. of the acid. No residue should be left when the sample is incinerated. The *acidity* may be determined by dissolving a weighed quantity of the acid in water and titrating with normal sodium hydroxide solution, phenolphthalein being used as indiator. Each cubic centimetre of alkali used corresponds to 0·075 grm. of tartaric acid. *Iron* may be detected by means of potassium ferrocyanide and estimated colorimetrically if present.

Tartaric acid is determined *gravimetrically* as potassium hydrogen tartrate. The following method is given by Allen: Two grams of the sample are dissolved in 20 c.c. of proof spirit (made by diluting methylated spirit to a density of 0·920), the solution filtered from any residue consisting of tartrates, and the filtrate made up to 45 c.c. with proof spirit. To this are added 5 c.c. of a cold saturated solution of potassium acetate in proof spirit and the liquid well stirred for ten minutes. Tartaric acid will be precipitated as crystalline potassium hydrogen tartrate. This is transferred to a beaker by means of a cold saturated solution of potassium hydrogen tartrate and digested in the cold for a few hours to remove any co-precipitated citrate. The precipitate is then filtered off on a weighed Gooch crucible, washed once with proof spirit, dried at 100° C. and weighed. The weight of the precipitate multiplied by 0·798 gives the quantity of tartaric acid in the 2 grms. taken. It is quicker to dissolve the precipitate in hot water and titrate it with decinormal sodium hydroxide in the presence of phenolphthalein; each cubic centimetre used corresponds to 0·015 grm. of tartaric acid.

Qualitative Tests for Tartaric Acid.—When tartaric acid is heated, it melts and chars, producing a smell like that of burnt sugar, and when heated with concentrated sulphuric acid it chars immediately. Citric acid chars only slowly with sulphuric acid and when heated alone it gives off aconitic acid ($C_6H_6O_6$). When silver nitrate is added to a neutralised solution of tartaric acid, a precipitate of silver tartrate is formed, which is soluble in ammonia; the ammoniacal solution gives a mirror of silver when warmed. Citric acid reacts similarly, except that it does not give a mirror. If a carefully neutralised cold solution of tartaric acid be treated with a solution of calcium chloride, a precipitate of calcium tartrate is formed. If this precipitate is filtered off and washed, it dissolves in acetic acid and in sodium hydroxide solution if free from carbonate. When the solution in alkali is boiled, the tartrate is reprecipitated. This test distinguishes calcium tartrate from calcium oxalate. When a citrate is treated with a cold solution of calcium chloride no precipitate is formed, but when the solution is boiled, calcium citrate separates out, but

redissolves on cooling. When a moderately concentrated solution of a tartrate is treated with potassium chloride and acetic acid, a precipitate of potassium hydrogen tartrate is formed, citric acid giving no precipitate under these conditions. If a drop of ferrous sulphate solution be added to a dilute solution of tartaric acid or of a soluble tartrate, and then a few drops of hydrogen peroxide, followed by excess of sodium hydroxide, a violet colour is produced, which is discharged by sulphurous acid. According to Fenton (*Commercial Organic Analysis*, Vol. I, p. 515, Allen), neither citric nor oxalic acid gives this reaction.

Cream of Tartar or *potassium hydrogen tartrate*, CHOH.COOH.CHOH.COOK, may contain neutral tartrates or calcium tartrate. Sulphates of potassium and calcium are also found occasionally. The *acidity* is determined by titration with normal or decinormal sodium hydroxide in the presence of phenolphthalein. Each c.c. of normal alkali corresponds to 0·150 grm. of tartaric acid or 0·188 grm. of potassium hydrogen tartrate. Owing to the comparative insolubility of potassium hydrogen tartrate, a considerable volume of hot water is required to dissolve it; but since neutral tartrates are readily soluble, the solution may be partly neutralised, then boiled, allowed to cool and the titration completed.

More detailed information is given by the following method of analysis: The acidity is determined by titration as already described. A second portion (1 or 2 grms.) is charred completely in a platinum dish at a low temperature (to prevent loss of potassium), the ash transferred to a dish or beaker, treated with a slight excess of decinormal sulphuric acid and the mixture boiled, after which the excess of acid is determined by titration with decinormal sodium hydroxide, methyl orange being used as indicator. This gives the alkalinity of the ash, and from this is subtracted the alkali required to neutralise the same weight of the original substance, both being expressed in terms of decinormal alkali; the difference is the neutralising power of the bases present as neutral tartrates. Each cubic centimetre of decinormal alkali is equivalent to 0·0113 grm. of potassium tartrate, 0·0094 grm. of calcium tartrate or 0·0075 grm. of tartaric acid present as neutral tartrate.

Allen (*Commercial Organic Analysis*, Vol. I, p. 522) gives also the following method, in which the whole of the tartaric acid present is precipitated as potassium hydrogen tartrate and determined by titration: About 3 grms. of the sample are weighed into a beaker and heated with a little water, after which a concentrated solution of neutral potassium oxalate is added, in sufficient quantity to react with all the calcium salts present and leave an excess of about 1·5 grms. of the salt. The mixture is heated for a short time, with frequent stirring, and then nearly neutralised with a solution of pure caustic potash. After heating for a short time, the liquid, which should not measure more than 40 c.c., is filtered and the residue washed well with water, the washings concentrated on the water-bath and added to the filtrate, the whole now measuring about 50 c.c. A solution of 2 grms. of citric acid in a little water is then added and the mixture stirred for ten minutes to precipitate the potassium hydrogen tartrate. This is then treated in the manner already described.

Goldenberg (*J. Soc. Dyers and Col.*, 1924, 260) uses the following method: 6 grms. of raw material containing 45 per cent. or more of tartaric acid, or 12 grms. of raw material containing less than 45 per cent., are digested for ten minutes with 18 c.c. of hydrochloric acid of 1·1 specific gravity, then rinsed into a 200 c.c. flask and the contents made up to the mark. This solution is filtered through a dry filter and 100 c.c. are boiled for 20 minutes with 10 c.c. of a 66 per cent. potassium carbonate solution (sp. gr. 1·48). When cool the alkaline solution is made up to 200 c.c., filtered from the precipitated calcium carbonate

through a dry filter, and 100 c.c. taken for the rest of the analysis. This volume is heated for 15 minutes in a porcelain dish, previously weighed after the addition of 3 c.c. of hydrochloric acid (1·1 sp. gr.), then made slightly alkaline with 10 per cent. potassium hydrate solution (using phenolphthalein as indicator), and concentrated until the solution weighs 40 grms. While the solution is still over the water-bath, 5 grms. of potassium chloride (KCl) and 5 c.c. of acetic acid, made up of equal quantities of glacial acetic acid and water, are added drop by drop. The dish is then taken from the water-bath, the contents stirred for five minutes and allowed to stand over night. The precipitated cream of tartar is carefully filtered off with the aid of a pump and washed with a saturated solution of the same salt. The washing is continued until 10 c.c. of the filtered liquid show the same acidity as 10 c.c. of the saturated solution.

The saturated solution used for washing is prepared by dissolving 1 grm. of pure cream of tartar in 800 c.c. of cold water and adding to this solution 4 c.c. of formaldehyde solution and 200 grms. of potassium chloride. When the latter has dissolved the liquid is diluted to 1,000 c.c. and filtered after standing 24 hours. It is essential that this saturated solution be prepared and used only at temperatures between 15° and 25° C.

Citric Acid, $CH_2COOH\ .\ C\,(OH)\ COOH\ .\ CH_2COOH$.

Commercial citric acid is liable to contain the same impurities as tartaric acid and is occasionally adulterated with tartaric acid. The qualitative differences between these two acids have already been described. The proportion of tartaric acid present is determined by the previous method. In the absence of other acids citric acid may be determined by titration with normal or decinormal sodium hydroxide in the presence of phenolphthalein, each cubic centimetre of the normal alkali neutralising 0·07 grm. of the crystallised acid, $C_6H_8O_7.H_2O$.

Lactic Acid, $CH_3\ .\ CHOH\ .\ COOH$.

This is a syrupy liquid having a specific gravity of 1·215. When distilled it is decomposed, forming acetaldehyde and other compounds, whilst when heated with dilute sulphuric acid acetaldehyde and formic acid are produced. When lactic acid is heated to a temperature of 130° C. lactic anhydride is formed, and at 150° C. a second anhydride or lactide is produced, both anhydrides occurring in commercial lactic acid ; their formulae are :

$$\left.\begin{array}{l} CH_3\ .\ CHOH\ .\ CO \\ CH_3\ .\ CHOH\ .\ CO \end{array}\right> O \qquad \text{and} \qquad \begin{array}{l} CH_3\ .\ CH{-}O{-}CO \\ \qquad\qquad\quad | \\ \quad\ \ CO{-}O{-}CH\ .\ CH_3 \end{array}$$

The Detection of Lactic Acid.—Lactic acid may be identified by distilling it with sulphuric acid and testing for acetaldehyde in the distillate. Déniges (*Analyst,* 1909, 369) states that the solution should not contain more than 2 per cent. of lactic acid. He applies the test in the following manner : 0·2 c.c. of a 2 per cent. solution of the acid is mixed with 2 c.c. of sulphuric acid (sp. gr. 1·84) in a test-tube and heated for 2 minutes in a water-bath. The contents of the tube are cooled and shaken with 2 drops of a 5 per cent. alcoholic solution of guaiacol or codeine. With the former a magenta coloration is produced with 0·01 mgrm. of lactic acid, whilst with codeine an orange-yellow colour is given. When the acid is oxidised by potassium bichromate and sulphuric acid, it gives rise to acetaldehyde, acetic acid and carbon dioxide ; this may be

made use of as a qualitative test. Gernuth (*Ind. Eng. Chem.*, 1927, **19**, 852) gives a test for detecting lactic acid in the presence of other acids, such as citric acid, tartaric acid, butyric acid, benzoic acid, salicylic acid, etc., based upon the fact that lactic acid or a solution of a lactate gives an orange or purple coloration when mixed with 15 per cent. potassium thiocyanate solution, the colour not being discharged by addition of mercuric chloride solution. If traces of iron are present, a coloration may be obtained on adding the thiocyanate, but is discharged at once by the mercuric chloride. The reaction is given by a 0·5 per cent. solution of lactic acid.

The Determination of Lactic Acid.—A weighed quantity of the acid is diluted with water to approximately decinormal strength. It is important to keep to this dilution because the proportions of lactic acid and anhydrides present vary with the dilution. Mineral acids such as sulphuric or hydrochloric acid are tested for and determined if present. In order to determine the *acidity*, 25 c.c. of the solution are titrated with decinormal sodium hydroxide in the presence of phenolphthalein until a red colour is produced. An excess of sodium hydroxide (30 c.c.) is then added and the cold mixture allowed to stand for 30 minutes. A known excess (40 c.c.) of decinormal sulphuric acid is added and after boiling the solution to expel carbon dioxide, the excess of acid is titrated back with decinormal sodium hydroxide in the presence of phenolphthalein. The difference between the total amount of alkali used and the quantity of sulphuric acid added corresponds to the free lactic acid and its anhydrides (1 c.c. ≡ 0·009 grm.). *Mineral acid*, if present, may be determined by the method of Thuau and Vidal (*Cuir.*, 1926, 311). The *sulphates* are precipitated with 95 per cent. alcohol, the solution filtered, and after evaporating off the alcohol, the free *sulphuric acid* is determined by precipitating with barium chloride. Alternatively, the total SO_3 and that in the ash may be determined, the difference representing free sulphuric acid. For free *hydrochloric acid* the sample is neutralised and incinerated and the chlorine content of the ash determined. The difference between this and the chlorine content of the ash of the original unneutralised sample gives the chlorine present as free hydrochloric acid.

CHAPTER VII.

INDICATORS AND THEIR HYDROGEN-ION CONCENTRATIONS (pH).

In the titration of acids and alkalis the following indicators are commonly used :

1. **Methyl Orange** (0·02 per cent. aqueous solution).—The solution is red in the presence of strong acids and yellow in the presence of alkalis, the neutral tint being orange. The range of pH values for which it can be used is 2·9 to 4·0. Methyl orange is unaffected by small quantities of carbon dioxide, but it is not sensitive in hot solutions. It is suitable for the titration of strong acids and strong bases, but not for weak ones.

2. **Methyl Red** (0·02 per cent. aqueous solution).—This indicator is yellow in alkaline solution and red in acid solutions. Since its range of pH values is 4·2 to 6·3, it is more sensitive to weak acids, such as carbonic acid, than methyl orange. The colour change is rather sharper than that of methyl orange, particularly when titrating acids with sodium hydroxide.

3. **Phenolphthalein** (1 per cent. alcoholic solution).—This solution is colourless in the presence of acids, including carbonic acid, and pink in the presence of alkalis, the range of pH values being 8·3 to 10. It is suitable for the titration of organic acids. It cannot be used with ammonia, or in the presence of ammonium salts, and is suitable for carbonates only in boiling solution.

4. **Litmus** (0·02 per cent. aqueous solution).—The colour change is from red (acid) to blue (alkaline), the pH range being 5 to 8. The neutral tint is violet. Litmus is slightly sensitive to carbonic acid, but gives a well-marked colour change with mineral acids, strong organic acids, alkaline hydroxides and ammonia.

5. **Cochineal** (a 1 per cent. alcoholic solution of extract of cochineal is used).—The indicator is yellowish-red in acid solutions, but its colour changes sharply to violet in the presence of alkalis, the colour range being pH 5 to 6. It is not suitable for titrating organic acids, but is very useful for solutions containing ammonium salts, such as the distillate obtained in a Kjeldahl determination of nitrogen.

6. **Congo Red** (0·02 per cent. aqueous solution).—This indicator is blue in acid solution and red in neutral or alkaline solution (pH 3 to 5). Since it is not sensitive to weak acids it may be used in the determination of mineral acids in the presence of weak organic acids.

Colorimetric Determination of pH Values.—In the colorimetric determination of pH values, a series of stable solutions of known pH value, which are easily prepared, are required together with a series of indicators showing well-defined colour changes covering the wide range of pH values from 1 to 11.

It is not advisable to employ solutions of strong acids or alkalis. Their solvent action on glass is an objection, and also the fact that very small quantities of either produce great changes in hydrogen-ion concentration. Solutions of hydrolysable salts, or of strong bases with weak acids or *vice versa,* are affected comparatively little by the addition of small quantities of acids or alkalis, and

are termed "*buffer solutions*." Sodium citrate, sodium borate and potassium dihydrogen phosphate are examples. By treating a suitable "buffer solution" with decinormal acid or alkali in suitable proportions, it is possible to obtain a solution of any desired *p*H value.

A suitable "Universal Buffer" is made by the *British Drug Houses, Ltd.*, from which solutions of *p*H value 2·7 to 11·4 may be prepared by the addition of either 0·2 *N* hydrochloric acid or 0·2 *N* sodium hydroxide as required by the formula $p\text{H} = 3{\cdot}1 \pm 0{\cdot}1185\ \text{V}$, where V = the number of cubic centimetres of acid or alkali which, added to 100 c.c. of the solution with subsequent dilution to 200 c.c., will give the *p*H value required, (+) signifying the addition of sodium hydroxide and (−) hydrochloric acid.

The following solutions (Evers, *Analyst*, 1921, 396) are also used:

A. 0·1 *N* Sodium citrate: 21·008 grms. pure citric acid are dissolved in 200 c.c. *N* sodium hydroxide solution and the solution made up to 1 litre with recently-boiled distilled water.

B. 0·2 *N* Sodium borate: 12·404 grms. boric acid are dissolved in 100 c.c. *N* sodium hydroxide and the solution made up to 1 litre as in *A*.

C. *M*/15 Potassium dihydrogen phosphate: 9·078 grms. of the pure salt are dissolved in water and the solution made up to 1 litre.

D. *M*/15 Disodium hydrogen phosphate: 23·870 grms. of the pure salt are dissolved in water and the solution made up to 1 litre.

In addition, decinormal solutions of hydrochloric acid and carbonate-free sodium hydroxide are required. The solutions are mixed in test-tubes of uniform size according to the quantities given in the following tables based upon the figures given by Evers:

Series I.—*p*H 1·2–2·8.

*p*H, . .	1·2	1·4	1·6	1·8	2·0	2·2	2·4	2·6	2·8
c.c. *A*, . .	1·2	2·0	2·5	2·85	3·1	3·3	3·45	3·65	3·85
c.c. *N*/10 HCl, .	8·8	8·0	7·5	7·15	6·9	6·7	6·55	6·35	6·15

Series II.—*p*H 3·0–5·0.

*p*H, . .	3·0	3·2	3·4	3·6	3·8	4·0	4·2	4·4	4·6	4·8	5·0
c.c. *A*, . .	4·05	4·3	4·55	4·8	5·2	5·6	6·1	6·8	7·7	8·8	10·2
c.c. *N*/10 HCl, .	5·95	5·7	5·45	5·2	4·8	4·4	3·9	3·2	2·3	1·2	0·5

Series III.—*p*H 5·2–6·8.

*p*H, ...	5·2	5·4	5·6	5·8	6·0
c.c. *A*, ...	8·4	7·6	6·9	6·3	6·0
c.c. *N*/10 NaOH, . .	1·4	2·35	3·1	3·7	4·0
*p*H, ...	6·2	6·4	6·6	6·8	
c.c. *C*, ...	8·2	7·2	6·2	5·0	
c.c. *D*, ...	1·8	2·8	3·8	4·7	

Series IV.—*p*H 7·0–8·4.

*p*H, ...	7·0	7·2	7·4	7·6	7·8
c.c. *C*, ...	4·0	2·8	2·0	1·4	0·8
c.c. *D*, ...	6·0	7·2	8·0	8·6	9·2
*p*H, ...	8·0	8·2	8·4		
c.c. *B*, ...	5·5	5·85	6·2		
c.c. *N*/10 NaOH, . .	4·5	4·15	3·8		

Series V.—*p*H 8·6–11.

*p*H, . . .	8·6	8·8	9·0	9·2					
c.c. *B*, . . .	6·8	7·5	8·5	9·8					
c.c. *N*/10 HCl, .	3·2	2·5	1·5	0·2					
*p*H, . . .	9·4	9·6	9·8	10·0	10·2	10·4	10·6	10·8	11·0
c.c. *B*, . . .	8·7	7·4	6·4	5·95	5·6	5·4	5·3	5·2	5·0
c.c. *N*/10 NaOH, .	1·3	2·6	3·6	4·05	4·4	4·6	4·7	4·8	5·0

A series of tubes is prepared in the foregoing manner, the *p*H values of which cover the colour change range of the selected indicator (a list of suitable indicators is given below), and 5 drops of the indicator solution are added to each tube. The tubes are labelled with their *p*H values and sealed off in a blowpipe flame. They are then placed in sequence in test-tube stands and kept in a dark cupboard.

The following indicators may be employed in the preparation of the standard tubes :

Series.	*p*H Range.	Indicator.	Concentration of Indicator.
I.	1·2 – 2·8	Thymol Blue.	0·04 per cent. aqueous solution.
II.	3·0 – 5·0	Congo Red.	0·02 ,, ,,
III.	5·2 – 6·8	Bromocresol Purple.	0·04 ,, ,,
IV.	6·8 – 8·4	Phenol Red.	0·02 ,, ,,
V.	8·3 –11·0	Phenolthymolphthalein.	0·04 ,, alcoholic solution.

10 c.c. of the liquid to be tested are pipetted into a test-tube of similar size to those containing the standards and first tested by the addition of 2–3 drops of B.D.H. Universal Indicator to determine the approximate *p*H value. The colour variation of this indicator with change of *p*H value is as follows :

*p*H 3	Red.	*p*H 7	Greenish-yellow.
4	Deeper red.	8	Green.
5	Orange-red	9	Greenish-blue.
6	Orange-yellow.	10	Violet.
		11	Deep reddish-violet.

The approximate pH value having been obtained in this manner, 10 c.c. of the liquid under examination are pipetted into a test-tube and 5 drops of the indicator covering the approximate pH value are added and the results compared with the standard tubes containing the same indicator. Thus, supposing that the Universal Indicator shows a bluish-green colour with the solution, this would indicate a pH value between 8 and 9. In this instance the colour reactions of both phenol red and phenolthymolphthalein with the liquid under examination would require to be determined and the results compared with the corresponding standards, viz., those towards the end of Series IV and those at the commencement of Series V.

The use of "buffer solutions" may be avoided by employing Michaelis' *m*-nitrophenol solution (*Analyst*, 1922, 89). In this method, 40 c.c. of 0·02 *N* sodium hydroxide solution (freshly prepared by diluting a carbonate-free normal sodium hydroxide solution) are pipetted into each of six Nesslerising cylinders. Quantities of 0·25, 0·29, 0·33, 0·38, 0·45 and 0·50 c.c. of a solution of *m*-nitrophenol (prepared from a 0·1 per cent. stock solution diluted 1 : 10) are added to the respective cylinders. A sufficient quantity of the *m*-nitrophenol indicator solution is then run, from a graduated pipette, into 40 c.c. of the liquid whose pH value is required, contained in a separate Nesslerising cylinder, until the colour of the contents of the latter exactly matches the colour of one of the standard cylinders. If V denotes the volume of indicator in the matched standard, V′ the volume of indicator added to the sample, then at ordinary temperatures

$$pH = 8{\cdot}33 + \log \frac{1 - V/V'}{V/V'}$$

where 8·33 is a constant for *m*-nitrophenol. Where considerable accuracy is required, corrections may have to be applied to compensate for temperature and salt and protein errors.

If Michaelis' method is adopted, it is convenient to construct a graph showing the variation of pH with V′, from which the pH value can be read off at a glance.

On adding the indicator to the sample in matching the colour with the standards used, some difficulty may be experienced when the liquid under examination is coloured. If the liquid is very deeply coloured, the method is inapplicable and the determination will have to be made electrometrically. In the case of not too deeply coloured solutions the comparison is facilitated by means of a *comparator* box. This may be constructed from a cube of wood of 3½ inch sides, in which vertical borings are made extending nearly to the base of the cube, and of diameter sufficient to take the test-tubes or cylinders employed in the determination. Two holes are also bored horizontally and completely through the block and the vertical borings, so that it is possible to look through two pairs of test-tubes simultaneously. The diameter of the horizontal borings should be somewhat less than the diameter of the tubes or cylinders employed. The interior parts of the cube, and also the outside, should be stained a dull black, to avoid internal reflection. In one vertical boring is placed the test-tube containing the liquid under examination, to which the indicator has been added, and, in the boring immediately behind, is placed a similar tube containing water. In the other pair of vertical borings the standard tube, with which comparison is made, is placed in the front boring, and a tube containing some of the liquid under examination in the boring immediately behind. In this way the colour effect of the sample is compensated and the sample to which the indicator has been added may be compared with the standard without

interference by the colour of the liquid. Simple comparators (see fig. 36) are supplied by *British Drug Houses, Ltd.*

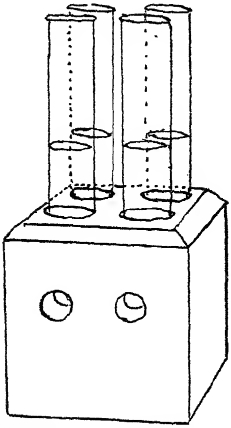


Fig. 36.—Comparator Set.

It is not necessary to make up a fresh set of standards for every test. If the test-tubes containing the standards are sealed and kept in the dark, these will remain unchanged for a long time. The "*Capillator Method*" devised by *British Drug Houses, Ltd.*, is very useful. The capillator consists of a series of capillary tubes filled with "buffer solutions" containing an indicator. The tubes are mounted in sets on white cards, each being marked with its exact *p*H value. A slot is provided in the card, so that by holding it up, colour comparisons can be made by transmitted light, whereas by viewing against the white background of the card, comparisons may be made by reflected light. The *p*H determination is made by using a capillary tube as a pipette and measuring with it equal volumes of liquid and indicator, mixing the two in a watch glass, and then drawing the mixed liquids back into the capillary tube. The colour of the mixed liquids is then matched against the capillator standards. A "compensator" is supplied for use with dark-coloured liquids. The special indicators used are:

Indicators for Use with the Capillator.

Thymol Blue,	*p*H 1·2 to 2·8
Bromophenol Blue,	*p*H 2·8 to 4·6
Bromocresol Green,	*p*H 3·6 to 5·2
Bromocresol Purple,	*p*H 5·2 to 6·8
Bromothymol Blue,	*p*H 6·0 to 7·6
Phenol Red,	*p*H 6·8 to 8·4
Cresol Red,	*p*H 7·2 to 8·8
Thymol Blue,	*p*H 8·0 to 9·6
B.D.H. Soil Indicator,	*p*H 4·0 to 8·0
B.D.H. "Four-Eleven" Indicator,	*p*H 4·0 to 11·0

Determination of the Acidity or Alkalinity of Commercial Samples.—When a large number of samples have to be compared for acidity or alkalinity, *e.g.* starch, gelatine, tanning liquors, etc., the colorimetric method for the determination of *p*H affords the simplest and readiest method. 10 c.c.-portions of solutions or suspensions of the samples of known concentrations are pipetted into test-tubes and 5 drops of the indicators covering the expected hydrion concentrations are added to the tubes and the resulting mixtures matched with the standards. Or, the method of Michaelis may be employed, although an additional calculation is necessary in this case if the graphical method (see before) is not employed.

Every pure salt, when in solution, should give a definite *p*H value for a given concentration. For salts formed from strong acids and strong bases, the *p*H values of their solutions will be about 7. For salts formed by the combination of a weak acid and a strong base the *p*H value will be greater than 7; and for salts of strong acids with weak bases the *p*H value will be less than 7.

In the titration of acids, bases or salts which are hydrolysed in aqueous

solution, the choice of an indicator is governed by the pH value at the end-point of the titration, which is represented by the symbol pT. Lizius and Evers (*Analyst*, 1922, 331) have determined pT for a large number of acids and bases in decinormal solution. The values are given in the following table, together with the indicators which are suitable for the titration.

Acids.	pT.	*Indicators.*	*End Colour.*
Hydrochloric acid, Hydrobromic acid, Hydriodic acid, Sulphuric acid	7·0	Methylthymol blue. Methyl red. Bromophenol blue.	Yellow. Orange. Green.
Nitric acid,	7·5	Phenol red.	Orange.
Benzoic acid,	7·6	,,	,,
Formic acid,	7·8	,,	,,
Lactic acid,	7·8	,,	,,
Oxalic acid,	8·0	,,	Red.
Tartaric acid,	8·1	,,	,,
Boric acid with glycerin,	8·6	Thymol blue or phenol violet.	Green.
Acetic acid,	8·8	,, ,, ,,	Blue.
Citric acid, Oleic acid,	9·5	Phenol violet or phenolthymolphthalein.	Violet.
Phenol,	12·0	Too weak for titration.	
Bases.			
Strong bases,	7·0	Methyl thymol blue, or methyl red, or bromophenol blue.	Yellow. Orange. Green.
Ammonia,	5·2	Methyl red.	Orange.
Pyridine,	3·6	Bromophenol blue.	Green.
Aniline,	2·8	,,	,,
Salts.			
Borax,	5·2	Methyl red.	Orange.
Sodium carbonate to bicarbonate,	8·4	Phenol violet or thymol blue.	Yellow.
Sodium phenate,	6·5	Phenol red.	,,
Sodium dihydrogen phosphate to acid salt,	4·5	Methyl red.	Red to maximum colour.
Sodium acid phosphate to normal salt,	9·1	Thymol blue or phenol violet.	Blue to standard colour.

CHAPTER VIII.

ALKALIS.

Sodium Hydroxide (*Caustic Soda*).

The impurities present in commercial sodium hydroxide are chiefly carbonates, chlorides and sulphates. Sulphides, silicates, compounds of iron or calcium are of rarer occurrence. These impurities are identified in the usual manner.

The analysis is carried out in the following manner: A weighed portion of the sample (from 4 to 5 grms.) is dissolved in water free from carbon dioxide. If *insoluble matter* is present it may be filtered off on a Gooch crucible and weighed. The solution is made up to one litre with carbon dioxide-free distilled water. 50 c.c. of this solution are titrated with decinormal acid in the presence of methyl orange. This gives the *total alkali* present. Another 50 c.c. are placed in a 100 c.c. flask, some barium chloride solution is added and the mixture diluted to 100 c.c. with carbon dioxide-free water. It is then mixed well and filtered rapidly. A portion of the filtrate (50 c.c.) is titrated with decinormal acid in the presence of phenolphthalein. This gives the *alkali* present *as sodium hydroxide*, the difference between this and the total alkali being calculated to *sodium carbonate*.

Sodium hydroxide and sodium carbonate when present together in a solution, may be determined also by titration with decinormal hydrochloric acid, first in the presence of phenolphthalein and then after addition of methyl orange. If hydrochloric acid be added until the pink colour of the phenolphthalein is first discharged, the whole of the hydroxide will have been neutralised and the carbonate converted into bicarbonate:

$$NaOH + HCl = NaCl + H_2O,$$
$$Na_2CO_3 + HCl = NaCl + NaHCO_3.$$

If now methyl orange is added and the titration continued until an orange tint is produced, the volume of acid used in the second titration will be that required to neutralise the bicarbonate formed from the sodium carbonate during the first part of the titration. Hence twice this volume will be equivalent to the sodium carbonate originally present, and the difference between this and the total acid used will give the sodium hydroxide. For example, if 50 c.c. of the solution required 15 c.c. of decinormal acid to discharge the pink colour of the phenolphthalein and a further 5 c.c. to produce the colour change in methyl orange, then

$$(5 \times 2) \times 0{\cdot}0053 \text{ grm.} = \text{sodium carbonate},$$
$$(20 - 10) \times 0{\cdot}004 \text{ grm.} = \text{sodium hydroxide}.$$

Potassium Hydroxide (*Caustic Potash*).

Caustic potash is analysed in the same way as sodium hydroxide. The approximate analysis of both may be made by taking the specific gravity of an aqueous solution of known concentration.

Sodium Carbonate.

Commercial sodium carbonate is obtainable in a number of forms, viz.:

"*Soda Ash*," crude unrefined material containing sodium hydroxide, sulphate, sulphite, chloride and iron and alumina.

"*Pure Alkali*," refined anhydrous sodium carbonate containing 98–99 per cent. Na_2CO_3.

"*Washing Soda*," containing 63 per cent. moisture and varying amounts of chlorides and sulphates.

"*Crystal Soda*," consisting of smaller crystals than washing soda and of a higher degree of purity.

"*Sesquicarbonate of Soda*," a double salt of the formula $Na_2CO_3.NaHCO_3.2\,H_2O$, generally purer than soda crystals. Some typical analyses of these products are given in the following table :

	48 per cent.	58 per cent.	Pure Ammonia Alkali.	Soda Crystals.	Crystal Soda.	Sesqui-carbonate.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Sodium carbonate,	60·64	98·72	98·94	34·22	81·92	46·90
Sodium bicarbonate,	...	...	...	...	...	37·17
Sodium sulphate,	4·35	0·20	0·20	2·54	0·18	...
Sodium hydrate,	1·29	...	...	0·10	...	...
Sodium chloride,	28·34	0·54	0·36	0·27	0·24	0·29
Ferric oxide,	trace	0·04	...	...	...	...
Alumina,	1·12	0·01	...	...	...	...
Silica,	0·00	0·09	0·09	0·03	...	...
Water,	4·26	0·26	0·38	62·84	17·66	15·64

For the purposes for which sodium carbonate is generally used, the presence of traces of sulphates and chlorides is not of importance. If, however, a qualitative examination shows that the amounts present are appreciable, they should be determined. The quantitative analysis of sodium carbonate is carried out by the method described for the analysis of commercial caustic soda.

Moisture Content.—A weighed quantity of the finely powdered sample is heated carefully on a sand bath until no further diminution in weight is observed.

Total Alkalinity.—The total alkalinity is determined by titration with decinormal hydrochloric or sulphuric acid using methyl orange as indicator.

Alkalinity Due to Acid and Normal Carbonates.—To 25 c.c. of a solution of the sample prepared in the same manner as for caustic soda, a known volume of decinormal solution of sodium hydroxide is added, followed by a solution of barium chloride in excess of that required to precipitate the carbonate. The excess hydroxide remaining is then determined by titration with decinormal acid, using phenolphthalein as indicator (Winkler). Then, if

t = total alkalinity of 25 c.c. of the sample as c.c. $N/10$ acid,

t_1 = c.c. $N/10$ NaOH added,

t_2 = c.c. $N/10$ acid used in final titration,

$(t + t_2 - t_1) \times 0{\cdot}0053$ = grms. sodium carbonate,

$(t_1 - t_2) \times 0{\cdot}0084$ = grms. sodium bicarbonate.

Potassium Carbonate.

Potassium carbonate is analysed in the same manner as sodium carbonate.

Ammonia.

The impurities frequently present in commercial ammonia solutions are chlorides, nitrates, sulphates, sulphides, pyridine and iron compounds.

The specific gravity is determined usually by means of a hydrometer and the corresponding ammonia content obtained from a specific gravity table such as that of Lunge and Wiernik given below.

SPECIFIC GRAVITY OF AMMONIA SOLUTIONS AT 15° C.

(Lunge and Wiernik.)

Specific Gravity, 15° C.	Per cent. NH_3.	Grms. NH_3 per litre.	Correction of Specific Gravity for +1° C.	Specific Gravity, 15° C.	Per cent. NH_3.	Grms. NH_3 per litre.	Correction of Specific Gravity for +1° C.
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

Total Solids.—The total solids are determined by evaporating 50-100 grms. of the sample (weighed in a stoppered weighing bottle) in a tared porcelain

basin from a water-bath, the operation being carried out in a fume cupboard. The evaporating basin is then transferred to an air oven and dried for 60 minutes at 120° C.

Total Alkalinity.—About 1·5 grms. of the sample are weighed in a stoppered weighing bottle and quickly transferred to a 500 c.c. graduated flask containing exactly 50 c.c. of normal sulphuric acid and the solution made up to the mark with distilled water. The excess acid remaining is then determined by titrating 50 c.c. portions of the liquid with decinormal alkali, cochineal being used as indicator. From this the acid which has combined with the alkali present is obtained by difference and its equivalent in terms of either NH_3 or NH_4OH calculated; the volume of acid which has entered into combination multiplied by 0·0017 corresponds to the NH_3 content and the factor 0·0034 gives the alkalinity in terms of NH_4OH.

Chlorides, Sulphates, Nitrates, Iron.—The residue remaining from the determination of the total solids is dissolved in water, unless only traces of these impurities are present, and the impurities determined by the methods already described under hydrochloric and sulphuric acids.

Pyridine.—Pyridine may be detected by acidifying a diluted portion of the sample with nitric acid. If present a yellow coloration will develop.

Ammonium Carbonate.

Three forms of "ammonium carbonate" can be prepared, viz., the normal ammonium carbonate, $(NH_4)_2CO_3.H_2O$, the acid carbonate, NH_4HCO_3, and the sesquicarbonate $(NH_4)_2CO_3 . 2\,NH_4HCO_3$. On exposure to the air the sesquicarbonate loses water and ammonia, yielding the acid carbonate. The ordinary commercial product sold as "ammonium carbonate" is largely a mixture of ammonium bicarbonate and ammonium carbamate, $NH_2.CO.ONH_4$. The analysis of ammonium carbonate is carried out on a solution of the sample in the same manner as in the examination of ammonia.

Lime.

Lime is sold either as such or in its hydrated form as $Ca(OH)_2$. It is met with in varying degrees of purity, the best samples containing not less than 95 per cent. of calcium oxide (CaO) or the hydroxide. Ordinary lime is supplied usually in bulk, the hydrated lime in bags.

For the analysis of lime the bulk sample is coned and quartered and the final sample then finely ground, if the original delivery is in lump form, and transferred to a stoppered bottle, the stopper of the bottle containing the stock samples being sealed with paraffin wax to prevent carbonisation of the lime by atmospheric carbon dioxide.

Total Alkalinity.—The calcium oxide content of the material, upon which the valuation of lime is based, is determined along with magnesium oxide by either of the following methods:

1 grm. of the powdered sample is weighed out into a mortar and triturated with a little distilled water free from carbon dioxide. The resulting paste is washed into a litre flask and the volume made up with carbonate-free water. The flask is sealed and allowed to stand for 12-16 hours, with occasional shaking, and the contents then allowed to settle.. 50 c.c.-portions of the clear liquid are pipetted into a titrating flask and the alkalinity determined by titration with decinormal hydrochloric acid. 1 c.c. of decinormal acid used in the titration is equivalent to 0·0028 grm. CaO.

The following method, employed by Henrick, is based upon the increased solubility of lime in aqueous solutions of cane sugar. 5 grms. of the powdered sample are transferred to a 500 c.c. graduated flask containing 10 c.c. of alcohol. The volume of the solution is made up to the mark with a 10 per cent. solution of cane sugar. The flask is stoppered and shaken for four hours in a mechanical shaker. After settling, 50 c.c.-portions of the clear solution are titrated with tenth-normal hydrochloric acid, using methyl orange as indicator.

The rate of settling of the insoluble matter is very slow when magnesia is present. Shaw, Macintyre and Underwood (*Ind. Eng. Chem.*, 1928, **20,** 312) recommend the following method for filtration: The ground lime is shaken with the sugar solution in a 500 c.c. Erlenmeyer flask, the stopper of which carries a soda-lime tube and a syphon connection. To the latter, and within the flask, a filter is connected, made from a cut-down pipette filled with dry cotton wool and covered with macerated filter paper. Aliquot parts of the solution are drawn off for titration by means of the syphon, any moisture in the filter being removed by the first portion. Another type of apparatus consists of a flask with a protected air connection and a measuring pipette with a three-way stop-cock at each end. Connected to the latter and within the flask is an alundum filtering thimble. The filtrate is drawn up in the pipette by suction.

Silica.—A solution of the sample is prepared in the following manner for the determination of silica and for the subsequent determinations: 5 grms. of the sample are weighed into a porcelain basin and about 50 c.c. of water added. Hydrochloric acid is added slowly and carefully until complete solution is obtained and the mixture evaporated on a water-bath and finally dried in a steam oven. The residue remaining is dissolved in dilute hydrochloric acid and any insoluble silica filtered off, dried, ignited and weighed.

Iron and Aluminium.—The filtrate and washings from the foregoing silica determination are collected in a 500 c.c. graduated flask and the volume made up with distilled water. 50 c.c. of this solution (representing 0·5 grm. of the sample) are pipetted into a beaker and a little hydrochloric acid added. The liquid is then made just alkaline by the addition of ammonia and boiled for a few minutes, any precipitated iron or aluminium hydroxide being filtered off and weighed. As a rule it is sufficient to record the combined weight of iron oxide and alumina found, but, if it is necessary to separate them, the following method should be adopted. After filtration and washing, the precipitate is transferred to a beaker with hot water and a little iron-free sodium peroxide is added to convert the alumina present into sodium aluminate. After boiling for a short period, the liquid is filtered and the unchanged iron oxide remaining on the filter is washed, dried, ignited and weighed. If the total iron and aluminium is also determined, the alumina is found by difference.

Total Calcium.—The filtrate from the hydroxides of iron and aluminium is heated to the boiling point and about 2 grms. of powdered ammonium oxalate added. The mixture is boiled for about 2 minutes and then filtered through a Gooch crucible, the precipitate being washed with hot water containing a little ammonia. The contents of the crucible are washed into a beaker, sulphuric acid added and the liberated oxalic acid titrated in the hot solution with decinormal potassium permanganate solution (1 c.c. $\equiv$ 0·0028 grm. CaO).

Magnesium.—The filtrate from the calcium determination is concentrated and some ammonia solution added. .The mixture is then acidified with hydrochloric acid, heated to the boiling point, and treated with an excess of sodium or ammonium phosphate, followed immediately by the addition of a volume of 10 per cent. ammonia solution equal to one-third of the volume of the liquid.

The liquid is then allowed to cool, and after standing for several hours is filtered through a tared Gooch crucible. The precipitate is washed with a 2·5 per cent. solution of ammonia, dried, and ignited very slowly, the temperature during ignition being raised gradually until the precipitate is white. The weight of the residual magnesium pyrophosphate is then determined and its equivalent in terms of magnesia obtained by multiplying the weight so found by 0·3621.

According to Treadwell (*Analytical Chemistry*, 1919, Vol. II., p. 67) correct results are obtained by following the foregoing procedure, but attention is directed to the importance of the slow ignition of the precipitate, otherwise it is almost impossible to obtain the white pyrophosphate.

The determination of the magnesium may also be made by the following method due to Gibbs (*Treadwell*). The filtrate from the calcium determination is neutralised by the addition of ammonia and any excess of the latter boiled off. A normal solution of microcosmic salt is added until no further precipitation takes place. A 10 per cent. ammonia solution is then added to the boiling liquid, with constant stirring, the amount added being about one-third the volume of the liquid. After standing 2-3 hours, the clear supernatant liquid is filtered off through a tared Gooch crucible, the precipitate washed three times by decantation with a 2·5 per cent. solution of ammonia and then transferred to the filter and again washed with the dilute ammonia solution. The precipitate is then dried in an oven and ignited slowly until no further evolution of ammonia occurs. At this stage the rate of heating may be increased until the residue is perfectly white. The crucible is cooled in a desiccator and weighed.

Sulphates.—For the determination of sulphates, 50 c.c. of the original aqueous solution of the sample are boiled and a slight excess of barium chloride added to the boiling liquid, the boiling being continued for about 5 minutes. The liquid is then allowed to stand for some time and the supernatant liquid passed through a filter; the residual barium sulphate is then washed by decantation through a tared Gooch crucible. The residue in the filter is washed, dried, and the weight multiplied by 0·5833 to convert it into terms of calcium sulphate.

Carbonates.—These may be determined directly, but can be deduced from the difference between the total and free lime after allowing for any calcium present as sulphate.

Borax, $Na_2B_4O_7 . 10\,H_2O$.

Borax is the sodium salt of tetraboric acid, which is a derivative of orthoboric acid :

$$4\,B(OH)_3 = H_2B_4O_7 + 5\,H_2O.$$

It is prepared by recrystallising native borax or by treating boric acid with sodium carbonate. It is a colourless crystalline substance, readily soluble in water, and its aqueous solution has an alkaline reaction owing to hydrolysis in accordance with the equation

$$Na_2B_4O_7 + H_2O \rightleftarrows NaOH + NaHB_4O_7.$$

When heated, borax swells and loses its water of crystallisation, and if the heating be continued, fuses with the formation of a colourless liquid which sets to a glass-like solid on cooling. The chief impurities of commercial borax are sodium chloride, sodium sulphate and sodium carbonate.

Chlorides and *sulphates* are tested for in the usual manner, and determined if present. *Sodium carbonate* is indicated if the total alkali (Na_2O) is in excess

of that required by the boric acid. When sodium carbonate is present, the sample will give off carbon dioxide when treated with hydrochloric acid, and this may be identified in the usual manner. The carbon dioxide may be determined by the method of Hepburn, which is described later (page 291).

Total Alkalinity.—10 grms. of the sample are dissolved in carbon dioxide-free water and the solution diluted to one litre. Since boric acid has no action on methyl orange, the total alkali present can be determined by titration with decinormal hydrochloric acid in the presence of this indicator, and in the absence of sodium carbonate the borax may be calculated.

To the titrated solution is now added about one-third of its volume of glycerin, previously made neutral to phenolphthalein. The solution contains the boric acid in the free state, and also carbonic acid if the sample contained sodium carbonate. Boric acid cannot be titrated in an aqueous solution owing to the hydrolysis of the sodium salt, but in the presence of sufficient glycerol a definite end-point is obtained, the appearance of the pink phenolphthalein colour corresponding to the formation of sodium metaborate, $NaBO_2$. The neutralised solution is boiled for a few minutes to expel carbon dioxide. It is then cooled, a few more drops of phenolphthalein added and more decinormal sodium hydroxide run in until a faint pink colour is obtained. Each cubic centimetre of alkali corresponds to 0·0062 grm. of boric acid, H_3BO_3, or 0·0035 grm. of boric anhydride, B_2O_3, or 0·00503 grm. of anhydrous borax, $Na_2B_4O_7$, or 0·00954 grm. of crystalline borax, $Na_2B_4O_7.10\,H_2O$. Each cubic centimetre of decinormal acid used in the first titration corresponds to 0·01908 grm. of crystalline borax or 0·01007 grm. of $Na_2B_4O_7$.

From the equation

$$Na_2B_4O_7 + 2\,HCl + 5\,H_2O = 2\,NaCl + 4\,H_3BO_3,$$

it is seen that Na_2O is equivalent to $4\,H_3BO_3$ or $2\,B_2O_3$.

Crystalline and anhydrous borax contain the following percentages of boric anhydride and sodium oxide :

	Sodium Oxide, Na_2O.	Boric Anhydride, B_2O_3.	Ratio $\frac{B_2O_3}{Na_2O}$
$Na_2B_4O_7.10\,H_2O$, . . .	16·25	36·52	2·247
$Na_2B_4O_7$, ...	30·79	69·20	2·247

If the percentage of boric anhydride found by the second titration agrees with the sodium oxide found in the first titration, no sodium carbonate is present and the sample is pure, the difference between the hydrated borax found and 100 being excess moisture. The percentage of water in crystalline borax is 47·18. This may be determined as a check by carefully heating a weighed quantity of the sample on a sand bath until no more weight is lost.

The test given by the British Pharmacopoeia is simple and trustworthy in the absence of carbonates. 2 grms. of the salt, dissolved in water, should require 10·4 c.c. of normal sulphuric acid for neutralisation in the presence of methyl orange ; and if to this neutralised solution an equal volume of glycerol is added, 20·8 c.c. of normal sodium hydroxide solution should be required for neutralisation in the presence of phenolphthalein.

Determination of Borax and Boric Acid in Size.—The determination of boric acid in complex organic mixtures is made by the following process : About 10

grms. of the substance are moistened with sodium hydroxide solution and charred completely in a platinum dish; sodium hydroxide is added to ensure that no free boric acid is present, since this might be lost during incineration. Whilst the mixture must be completely charred, it should not be burnt to an ash. The charred residue is extracted with water and made acid with hydrochloric acid, and before proceeding with the determination, a qualitative test for boric acid should be made with turmeric paper, the moist paper becoming rose-red on drying. The acid mixture is washed into a 100 c.c. flask, about 0·5 grm. of calcium chloride is added, a drop or two of phenolphthalein, and then dilute sodium hydroxide solution until a pink colour is produced. After adding 25 c.c. of lime water, the contents of the flask are made up to 100 c.c., mixed well and filtered. The object of the calcium chloride and lime water is to ensure the precipitation of phosphates and other acids, which otherwise might afterwards be titrated with the boric acid. A measured portion of the filtrate is made exactly neutral to methyl orange. When this is done no acids other than boric acid and carbonic acid are present in the free state. The latter is removed by boiling the solution for a few minutes, after which the solution is cooled, and about half its volume of glycerin, neutralised to phenolphthalein, is added. The boric acid is now determined by adding phenolphthalein and titrating with decinormal sodium hydroxide as already described.

Sodium Sulphide.

Commercial sodium sulphide may be in the form of crystals of the composition $Na_2S \cdot 9\,H_2O$ or a fused mass containing a variable proportion of water. Its aqueous solution is strongly alkaline in reaction owing to the liberation of sodium hydroxide by hydrolysis. When the solution is treated with an acid, sulphuretted hydrogen is given off and in most cases sulphur is precipitated. The latter may be due to the presence of either polysulphides or thiosulphates of sodium. Sodium sulphide may be made by heating sulphur with sodium hydroxide or its solution; in this case sodium thiosulphate would always be formed in accordance with the equations

$$3\,S + 4\,NaOH = 2\,Na_2S + SO_2 + 2\,H_2O,$$
$$SO_2 + 2\,NaOH = Na_2SO_3 + H_2O,$$
$$Na_2SO_3 + S = Na_2S_2O_3.$$

The chief qualitative tests for sulphides are the formation of a black colour or precipitate of lead sulphide with a solution of lead acetate and of a violet colour with a fresh solution of sodium nitroprusside. The presence of thiosulphate can be detected in the manner described later.

Analysis.—Owing to its deliquescent nature, the sampling of bulk lots of sodium sulphide presents some difficulty and samples should be kept in well stoppered bottles until the analysis is completed.

A weighed quantity of the sample is treated with water and the insoluble matter filtered off on a Gooch crucible, dried and weighed. This may contain compounds of calcium and iron, which are determined if necessary by the usual methods.

Sodium sulphide may be determined by titration with decinormal hydrochloric or sulphuric acid in the presence of methyl red or methyl orange, since neither sodium sulphydrate nor sulphuretted hydrogen affect these indicators in dilute solutions. From 10 to 12 grms. of the sulphide are weighed and dissolved in a litre of distilled water. A portion of this solution is titrated with

decinormal acid until the colour of methyl orange is just changed. Each cubic centimetre of acid used corresponds to 0·012 grm. of crystalline sodium sulphide, $Na_2S . 9 H_2O$. This method is only approximate and sodium sulphydrate and polysulphide are included with the sodium sulphide. Another method which fails also to distinguish between these compounds is to decompose the solution with acid and determine the liberated sulphuretted hydrogen by means of decinormal iodine solution. A measured quantity of decinormal iodine solution is acidified with hydrochloric acid and 25 c.c. of the sulphide solution are run into the mixture slowly, with constant stirring. The excess of iodine is then determined by means of decinormal sodium thiosulphate solution. The reactions are

$$Na_2S + 2\,HCl = 2\,NaCl + H_2S,$$
$$NaSH + HCl = NaCl + H_2S,$$
$$H_2S + I_2 = 2\,HI + S.$$

It must be noted that sulphuretted hydrogen cannot be titrated directly by the addition of iodine solution.

The differentiation between sodium sulphide and *sodium sulphydrate* can be made if required by a method given by Atkin (*J.L.T.C.*, 1922, 239), who states that a solution of sodium sulphydrate of $N/15$ concentration has an alkalinity corresponding to $p\text{H} = 10{\cdot}0$. If the alkalinity be reduced by the addition of acid, sulphuretted hydrogen is formed, but practically no sulphydrate is decomposed, except the small amount due to hydrolysis, if the solution be at $p\text{H} = 10$ or higher. Now an $N/15$ solution of sodium hydrosulphide is produced from an $M/15$ solution of sodium sulphide :

$$Na_2S + H_2O \rightleftarrows NaOH + NaHS.$$

The sodium hydroxide can be neutralised, and if precautions be taken not to let the alkalinity fall below $p\text{H} = 10$, practically no sulphydrate will be decomposed. Atkin based a method of titration upon these facts, using a solution which is either $N/15$ NaSH or $M/15$ Na_2S. This solution is titrated with decinormal acid to $p\text{H} = 10$, using a comparator and thymolphthalein as indicator. In this way the sodium hydroxide is neutralised, leaving sodium hydrosulphide and sodium chloride in solution. Neutralised formaldehyde is then added to liberate sodium hydroxide from the sulphydrate :

$$NaSH + H_2O + HCHO = NaOH + HCH\,(SH)\,(OH).$$

This alkali is again titrated and is a measure of the sodium sulphydrate present.

Sodium thiosulphate may be determined by the method of Lombard and Bravo (*J. Soc. Dyers and Col.*, 1926, 357). 10 grms. of the sample are dissolved in freshly distilled water, the solution diluted to 1 litre and 20 c.c. added slowly to 50 c.c. of decinormal iodine solution diluted with 100 c.c. of water and acidified with acetic acid. The excess of iodine is determined by titration with decinormal sodium thiosulphate ($= a$ c.c.). In order to determine the iodine used up by the thiosulphate, 100 c.c. of the original solution are treated with 100 c.c. of $N/5$ zinc sulphate solution, the mixture filtered, and 40 c.c. of the filtrate ($=$ 20 c.c. of original solution) titrated with decinormal iodine ($= b$ c.c.).

Then $50 - (a + b) = x$, where x is the number of cubic centimetres of $N/10$ iodine used by the sodium sulphide in 20 c.c. of the solution.

Treadwell recommends shaking the solution with freshly precipitated cadmium carbonate, which removes both the sulphide and sulphydrate. The mixture is filtered and the filtrate titrated with iodine solution.

Sodium sulphide may be determined by direct titration with a standard solution of zinc sulphate. A decinormal solution is made by dissolving 14·38 grms. of zinc sulphate, $ZnSO_4.7\,H_2O$, in water, adding ammonia until the precipitate first formed is just dissolved, and then adding 50 grms. of ammonium chloride and diluting the solution to 1 litre with distilled water. Each cubic centimetre of this solution will decompose 0·012 grm. of crystalline sodium sulphide. An external indicator is required. This consists either of lead acetate solution or a freshly prepared solution of sodium nitroprusside. The latter gives a violet colour with soluble sulphides. In carrying out the titration the zinc sulphate solution is run from a burette into the solution of the sulphide, the mixture being well stirred after each addition. A drop of the liquid is taken out with a pointed glass rod and brought into contact with a drop of lead acetate solution placed on a filter paper. As long as any undecomposed sodium sulphide remains, a brown or black colour is produced.

Cantoni (*J. Soc. Dyers and Col.*, 1926, 322) bases a method for the analysis of sodium sulphide upon the reaction

$$2\,K_3AsO_3 + 3\,Na_2S + 6\,H_2SO_4 = As_2S_3 + 3\,Na_2SO_4 + 3\,K_2SO_4 + 6\,H_2O.$$

The solution of the sulphide is filtered and to a measured volume of the filtrate an excess of standard arsenite solution is added, the mixture acidified with 20 per cent. sulphuric acid and boiled gently for half an hour. After cooling, excess of sodium bicarbonate is added and the excess of arsenite determined by titration with iodine solution. The object of boiling is to decompose sulphites and thiosulphates.

Sodium Silicate.

Commercial sodium silicate has the composition $Na_2O\,.\,2\,SiO_2$, but other forms such as $Na_2O\,.\,4\,SiO_2$ are also prepared. The proportions of sodium oxide and silica may be determined as follows: A weighed quantity of the substance is dissolved in water and the solution diluted to a definite volume. One portion of the solution is titrated with decinormal acid in the presence of methyl orange and the *total alkali* calculated. A second portion is acidified with hydrochloric acid and evaporated to dryness on a water-bath. The residue is treated with a little concentrated hydrochloric acid, dried and baked in an air bath or on a hot plate to dehydrate the silicic acid. The residue is then extracted with dilute hydrochloric acid, the *silica* filtered off, washed, ignited and weighed.

CHAPTER IX.

BLEACHING AGENTS.

Analysis of Sulphurous Acid and the Sulphites.

SULPHUR dioxide in aqueous solution is determined by titration with decinormal iodine solution:

$$I_2 + 2\,H_2O + SO_2 = 2\,HI + H_2SO_4.$$

The solution of sulphur dioxide may be run into a measured volume of decinormal iodine solution until the colour of the iodine disappears, or the blue colour of iodide of starch disappears if starch is used as an indicator. The sulphurous acid must be added slowly and with constant stirring. Iodine solution cannot be run into the sulphurous acid unless excess is used, since the oxidation is not complete. According to Treadwell the hydriodic acid which is formed reduces some of the sulphurous acid to sulphur:

$$SO_2 + 4\,HI = 2\,I_2 + 2\,H_2O + S.$$

The titration is made generally in the following manner: A suitable volume of the solution containing sulphur dioxide is run into a stoppered bottle containing a known quantity (excess) of decinormal iodine solution. The contents of the bottle are mixed and allowed to stand for a short time, after which the unused iodine is determined by titration with decinormal sodium thiosulphate. Each cubic centimetre of iodine which has disappeared corresponds to 0·0032 grm. of sulphur dioxide.

$$2\,Na_2S_2O_3 + I_2 = 2\,NaI + Na_2S_4O_6.$$

Sulphurous acid may be determined, also, by titration with decinormal sodium hydroxide solution, either phenolphthalein or methyl orange being used as indicator. The production of a pink colour in the presence of phenolphthalein corresponds to the equation

$$H_2SO_3 + 2\,NaOH = Na_2SO_3 + 2\,H_2O.$$

Since sodium bisulphite is acid to phenolphthalein, each cubic centimetre of alkali used is equivalent to 0·0032 grm. of sulphur dioxide. Sodium bisulphite is neutral towards methyl orange, but sulphurous acid changes the colour to red. If the titration is made in the presence of this indicator the reaction is

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O.$$

Thus only half as much alkali will be required as when phenolphthalein is used, and consequently the factor is 0·0064. Kedesky (*Chem. Zeit.*, 1914, **38**, 601) found that when titrating sulphurous acid with sodium hydroxide using methyl orange and phenolphthalein consecutively as indicators, the sharpness of the end-point could be increased by adding an excess of hydrogen peroxide after

the first titration. The effect of the hydrogen peroxide would be to change the sodium bisulphite produced in the first reaction to sodium hydrogen sulphate :

$$NaHSO_3 + H_2O_2 = NaHSO_4 + H_2O.$$

Kolthoff (*Chem. Weekblad.*, 1919, 1154) obtained a sharper end-point by adding barium nitrate towards the end of the second titration.

Sulphurous acid may also be determined by means of hydrogen peroxide by either of the following methods : (1) Adding an excess of standardised hydrogen peroxide and determining the unused residue by back-titration with potassium permanganate. (2) Adding neutralised hydrogen peroxide and titrating the sulphuric acid produced.

When the approximate strength of a solution of sulphurous acid is required, the specific gravity of the liquid at 15° C. may be taken and referred to the following table :

Specific Gravity.	Per cent. SO_2.	Specific Gravity.	Per cent. SO_2.
1·0028	0·5	1·0302	5·5
1·0056	1·0	1·0328	6·0
1·0085	1·5	1·0353	6·5
1·0113	2·0	1·0377	7·0
1·0141	2·5	1·0401	7·5
1·0168	3·0	1·0426	8·0
1·0194	3·5	1·0450	8·5
1·0221	4·0	1·0474	9·0
1·0248	4·5	1·0497	9·5
1·0275	5·0	1·0520	10·0

Sodium Sulphites.—There are three forms of commercial " sodium sulphite," which contain different percentages of sulphur dioxide, viz. :

Sodium sulphite, $Na_2SO_3 . 7 H_2O$,	25·40 per cent. SO_2.
Sodium bisulphite, $NaHSO_3$, .	61·54 ,, ,,
Sodium metabisulphite, $Na_2S_2O_5$,	67·37 ,, ,,

Since sodium sulphite is made by passing sulphur dioxide into a solution of the carbonate, the latter body may be present as an impurity, as well as sodium sulphate or sodium hydrogen sulphate, owing to the readiness with which sulphites are oxidised. For most textile purposes the percentage of *sulphur dioxide* is the most important consideration and small quantities of impurities are not of much importance. *Sodium carbonate* may be detected by the identification of carbon dioxide when the sample is treated with acid. *Sulphates*, if present, give an immediate precipitate with barium chloride in the presence of hydrochloric acid, barium sulphite being soluble in the acid ; but, in carrying out this test the sample should first be boiled with hydrochloric acid until all the sulphur dioxide has been expelled, and the barium chloride added to the boiling solution.

Sodium Bisulphite and Sodium Sulphite.—The examination of commercial sodium bisulphite is carried out commonly by titration either with sodium hydroxide or iodine in the manner described for sulphurous acid. In the iodine titration the solution of the bisulphite is run from a burette into a known volume of decinormal iodine solution containing hydrochloric acid or into an excess of iodine solution, the unused iodine being determined by back-titration.

There are errors inseparable from both of these methods. Sodium bisulphite generally contains both sodium hydrogen sulphate and normal sodium sulphite, whilst according to Harrison and Carroll (*J.S.C.I.*, 1925, 127 T) sodium metabisulphite may also be present. When bisulphites are determined by titration with alkali, bisulphates are included, whilst titration with iodine only gives the total sulphur dioxide present. Sulphites are also analysed by the iodine method. They do not as a rule contain either sulphurous acid or bisulphites, and the sources of error mentioned do not arise. The following methods have been proposed for dealing with mixtures of sulphurous acid, bisulphites and sulphites.

Titration with Alkali.—A measured volume of the solution is titrated with decinormal sodium hydroxide, methyl orange being added as indicator. When the solution is just neutral to methyl orange, all the free sulphurous acid exists as bisulphite. The volume of sodium hydroxide solution used is noted (a). Phenolphthalein is then added and the titration continued until a faint pink colour is obtained, indicating that the whole of the bisulphite has been changed to sulphite. The total volume of alkali used is again noted (b). Then

$$a \times 0{\cdot}0064 = \text{Free sulphurous acid } (SO_2).$$
$$(b - a) \times 0{\cdot}0032 = \text{Sulphur dioxide as bisulphite.}$$

It should be noted that when sodium bisulphite is present it also will be neutralised by the sodium hydroxide. This method is only suitable for mixtures of *sulphurous acid and bisulphites.*

Mixtures of *sodium sulphite and bisulphite* may be examined by a combination of the alkalimetric and iodometric methods, based upon the equations

$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O,$$
$$Na_2SO_3 + 2\,HCl = SO_2 + 2\,NaCl + H_2O,$$
$$SO_2 + I_2 + 2\,H_2O = H_2SO_4 + 2\,HI.$$

Kühl (*J.Soc.L.T.C.*, 1922, 199) proposed the following process in order to overcome the difficulty that *bisulphates* are included in the titration of bisulphites with alkali: 2 grms. of the sample are dissolved in water and titrated with normal sodium hydroxide solution in the presence of phenolphthalein (a c.c.), and then 10 c.c. of neutral 40 per cent. formaldehyde solution are added. This causes the liberation of sodium hydroxide in accordance with the equation

$$Na_2SO_3 + HCHO + H_2O = HCHO\,.\,NaHSO_3 + NaOH.$$

The liberated sodium hydroxide is determined by titration with normal hydrochloric acid (b c.c.).

$$1 \text{ c.c. } N\ HCl \equiv 0{\cdot}064 \text{ grm. } SO_2.$$

The following results are possible :

(1) If $a = b$, any impurities present are neutral salts such as sodium sulphate.

(2) If $a > b$, acid impurities are present and
$a - b$ is calculated to $NaHSO_4$.

(3) If $b > a$, normal sulphite is present and the difference
$b - a$ is calculated to Na_2SO_3.

Method of Harrison and Carroll for the Examination of Sodium Bisulphite (*J.S.C.I.*, 1925, 127 T).—The bisulphite is oxidised to bisulphate by means of hydrogen peroxide and the total sulphur dioxide is determined by titration with iodine.

Total Sulphur Dioxide.—About 0·25 grm. of the sample is weighed on a watch glass and dropped gently into a large beaker containing 50 c.c. of *N*/10 iodine solution and 100 c.c. of distilled water. When the bisulphite has dissolved, the unused iodine is determined by titration with *N*/10 sodium thiosulphate solution.

Sulphur Dioxide as Metabisulphite.—Exactly 10 c.c. of 20 vol. hydrogen peroxide are added to each of three flasks containing 50 c.c. of distilled water and 0·5 c.c. of a 0·2 per cent. solution of methyl orange. If necessary *N*/5 sodium hydroxide is added until only a faint red colour is visible. About 1 grm. of the sample is weighed and transferred to one of the flasks with a few cubic centimetres of water and the operation is repeated with the second flask. The flasks are then shaken and cooled if necessary. About 50 c.c. of water are added to the third flask, which represents the blank experiment, so that the concentration of the indicator is approximately the same as in the other two at the end of the titration. The contents of the two flasks containing the sodium bisulphite are then titrated with *N*/5 sodium hydroxide solution until the tints in all three are identical. The calculation is illustrated by the following examples :

Sample.	A.	B.	C.	D.	E.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total SO_2, ...	65·78	65·45	64·95	57·83	63·40
SO_2 present as metabisulphite, .	64·15	63·62	62·54	53·05	60·42

The difference between the total SO_2 and that present as metabisulphite is a measure of the normal sulphite. After determining the sodium sulphate the following values were calculated :

Sample.	A.	B.	C.	D.	E.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Sodium metabisulphite, $Na_2S_2O_5$,	95·23	94·45	92·86	78·76	89·69
Sodium sulphite, Na_2SO_3, . .	3·21	3·60	4·75	9·41	5·87
Sodium sulphate, Na_2SO_4, . .	1·61	1·91	2·41	9·82	4·12

The investigators conclude that the assumption that commercial bisulphites contain $NaHSO_3$ is incompatible with the results of these analyses, for if they did, the sum of the constituents in the foregoing examples would have exceeded 100 per cent. in every case.

Hydrosulphites.—Sodium hydrosulphite, $Na_2S_2O_4$, is a colourless powder which is readily soluble in water. Its aqueous solution is not very stable and breaks down gradually into a mixture of substances including sodium sulphite, sodium thiosulphate, sodium bisulphite and free sulphur. The addition of acid to the solution causes these changes to take place very rapidly, but in the presence of alkali the solution is much more stable. In the first two cases the

rate of decomposition increases with the temperature. An aqueous solution of sodium hydrosulphite undergoes "auto-oxidation" in accordance with the equation

$$2\,Na_2S_2O_4 = Na_2S_2O_3 + Na_2S_2O_5.$$

In the presence of caustic alkali this reaction becomes much slower and the metabisulphite reacts with two molecules of sodium hydroxide, thus

$$Na_2S_2O_5 + 2\,NaOH = 2\,Na_2SO_3 + H_2O.$$

When the hydrosulphite is exposed to air, sodium metabisulphite is gradually formed :

$$Na_2S_2O_4 + O = Na_2S_2O_5.$$

"Formosuls" are derivatives of sodium hydrosulphite and formaldehyde and are sodium salts of sulphoxylic acid formaldehyde.

Sodium sulphoxylate-formaldehyde (or "formosul") has the formula $NaHSO_2 . CH_2O . 2\,H_2O$. Such compounds are comparatively stable. When used in aqueous solution "formosul" does not exert its full reducing action until a temperature of 180° to 214° F. is reached. Basic zinc sulphoxylate-formaldehyde, $Zn\,(OH)\,HSO_2 . CH_2O$, or "zinc formosul," is still more stable than "formosul." It is insoluble in water but dissolves in dilute acids. It only exerts its full reducing action in a boiling acid solution. Normal zinc sulphoxylate-formaldehyde has the composition $Zn < \begin{matrix} HSO_2 . CH_2O \\ HSO_2 . CH_2O \end{matrix}$. It is soluble in water and dilute acids and the solutions are comparatively stable. It is insoluble in alkalis, being changed into the basic salt. Its solution is about one-third stronger as a reducing agent, owing to the fact that there is an extra sulphoxylate-formaldehyde radicle which replaces the hydroxyl group.

Analysis.—Knecht's Method (*J.S.C.I.*, 1915, 421).—Hydrosulphites are oxidised to sulphites by sodium chromate in the presence of an alkali, and the sodium sulphite is not oxidised further :

$$2\,Na_2CrO_4 + 3\,Na_2S_2O_4 + 2\,NaOH = 6\,Na_2SO_3 + Cr_2O_3 + H_2O.$$

From 0·1 to 0·2 grm. of the hydrosulphite is added to 20 c.c. of decinormal potassium bichromate solution made alkaline with sodium hydroxide. The precipitated oxide of chromium is filtered off, washed with water and converted into sodium bichromate by boiling with water and sodium peroxide. After boiling off the excess of hydrogen peroxide, the solution is cooled, acidified, and the bichromate determined by titration with decinormal sodium thiosulphate solution after addition of potassium iodide in the manner used for standardising solutions of potassium bichromate. Each cubic centimetre of decinormal sodium thiosulphate used corresponds to 0·00253 grm. of Cr_2O_3 and 1 grm. of Cr_2O_3 to 1·1447 grms. of $Na_2S_2O_4$. In Knecht's original method standard titanous chloride is used for the titration.

Merriman's Method (*J.S.C.I.*, 1923, 291).—When sodium hydrosulphite is treated with excess of formaldehyde, a mixture of sodium sulphoxylate-formaldehyde and sodium bisulphite-formaldehyde is produced :

$$Na_2S_2O_4 + 2\,CH_2O + 4\,H_2O = NaHSO_2 . CH_2O . 2\,H_2O + NaHSO_3 . CH_2O . H_2O.$$

Sodium sulphoxylate-formaldehyde reacts with iodine in neutral or acid solution, but the bisulphite compound remains unchanged :

$$NaHSO_2 . CH_2O . 2\,H_2O + 2\,I_2 = NaHSO_4 + CH_2O + 4\,HI.$$

The action of iodine on a solution of sodium hydrosulphite in the presence of excess of formaldehyde is thus :

$$Na_2S_2O_4 + 2\,CH_2O + 2\,I_2 + 4\,H_2O = NaHSO_4 + 4\,HI + CH_2O + NaHSO_3.CH_2O.H_2O.$$

Thus $Na_2S_2O_4 \equiv 4I$, and 1 c.c. $N/10$ iodine $\equiv$ 0·004352 grm. $Na_2S_2O_4$.

A litre flask is cut off at the neck about one inch above the mark and closed with a rubber bung. From 20 to 40 c.c. of formaldehyde (formalin) are placed in the flask, made up to rather less than 950 c.c. with distilled water and the liquid mixed. The hydrosulphite (10 grms.) is then introduced through a dry funnel with a wide stem. The funnel is washed down rapidly, the volume made up to 1000 c.c. with water, the bung replaced and the contents of the flask mixed. The titration is made by placing 100 c.c. of water in a beaker, then adding 20 c.c. of the hydrosulphite solution, followed by 50 c.c. of $N/10$ iodine solution. After two minutes the excess of iodine is determined by titration with decinormal sodium thiosulphate solution.

Wilkes' Method (*J.S.C.I.*, 1923, 356 T).—A mixture of potassium iodate and iodide is used, which gives iodine in accordance with the equation

$$HIO_3 + 5\,HI = 3\,I_2 + 3\,H_2O.$$

The reactions are :

(1) $3\,Na_2S_2O_4 + KIO_3 + 3\,H_2O = KI + 6\,NaHSO_3$,
(2) $6\,NaHSO_3 + KIO_3 + 5\,KI = 3\,I_2 + 3\,H_2O + 3\,Na_2SO_3 + 3\,K_2SO_3$,
(3) $3\,Na_2SO_3 + 3\,K_2SO_3 + 6\,H_2O + 6\,I_2 = 3\,Na_2SO_4 + 3\,K_2SO_4 + 12\,HI$,
(4) $12\,HI + 2\,KIO_3 = 2\,KI + 6\,I_2 + 6\,H_2O$.

Hence the oxidation of the sulphites may be ignored, and the effect of the hydrosulphite on the iodide and iodate is finally

$$3\,Na_2S_2O_4 + 4\,KIO_3 + 2\,KI = 3\,I_2 + 3\,Na_2SO_4 + 3\,K_2SO_4.$$

A litre flask is half filled with water, 6 grms. of potassium iodate and 10 grms. of potassium iodide are added and dissolved, after which 300 c.c. of $N/10$ thiosulphate solution are added and the flask filled with water to about 50 c.c. from the mark. About 2 grms. of hydrosulphite are introduced through a funnel with a short wide neck. The flask is first shaken so as to impart a whirling motion to the liquid, then it and the funnel are inclined to meet the weighing bottle so that when the latter is completely inverted it seals the mouth. This prevents the loss of any fine particles of hydrosulphite in the form of a cloud. The flask is then filled up to the mark and stoppered and shaken until the hydrosulphite is dissolved. The empty weighing bottle is re-weighed and the weight of the hydrosulphite determined by difference. The excess of thiosulphate is determined by titrating 100 c.c. with $N/10$ iodine solution. It is essential that, in weighing, the hydrosulphite be transferred from the sample bottle to the weighing bottle with a spatula and not by pouring, since in the latter case a partial separation of the salt generally used as a diluent occurs and inaccurate results are obtained.

Calculation.—

Weight of hydrosulphite taken, . .	2·0136 grms.
Mean titration, ...	7·24 c.c.
$N/10$ iodine for 1,000 c.c., . . .	72·4 c.c.

∴ $N/10$ thiosulphate absorbed by hydrosulphite reaction $= (300 - 72{\cdot}4) = 227{\cdot}6$ c.c.
Molecular weight of hydrosulphite = 174.

$$\therefore \text{Percentage of hydrosulphite} = \frac{174 \times 227{\cdot}6 \times 100}{2 \times 10{,}000 \times 2{\cdot}0136} = 98{\cdot}34\ \%.$$

Bollenbach's Method (*Analyst*, 1910, 140).—The hydrosulphite is oxidised by ferric ammonium sulphate, thus :

$$Fe_2(SO_4)_3 + Na_2S_2O_4 + H_2SO_4 = 2\ FeSO_4 + 2\ NaHSO_4 + 2\ SO_2.$$

The standardised iron solution is acidified with sulphuric acid and a few drops of potassium thiocyanate solution are added. The hydrosulphite solution is then run in until the red colour has almost disappeared. Two drops of a dilute solution of indigo carmine are now added and titration continued until the blue colour disappears.

Hydrosulphites may be determined rapidly with approximate accuracy by titration with indigo carmine solution prepared by dissolving 2 grms. of pure indigotin in concentrated sulphuric acid and diluting to one litre. The titration is made by placing 250 c.c. of this solution in a large porcelain dish or a flask and running in the hydrosulphite solution until a pale yellow colour is produced. The number of cubic centimetres used gives the hydrosulphite required to reduce 0·5 grm. of indigotin.

Hydrogen Peroxide.

Commercial hydrogen peroxide may contain the following impurities and bodies added as stabilisers : Acids such as oxalic, salicylic, phosphoric or sulphuric acid, glycerol, acetanilide, alcohol, magnesium chloride, fluorides, sodium chloride, sodium sulphate, and compounds of iron, barium, ammonium, magnesium, aluminium and silica. Sodium chloride and sodium sulphate reduce the stability of the solution, but magnesium chloride is added sometimes with the object of stimulating the bleaching action.

Acidity.—The acidity of commercial samples should not exceed 1·5 per cent. expressed as sulphuric acid. Acid is added to increase the stability of the solution. It is determined by titrating a measured volume of the sample with decinormal sodium hydroxide, phenolphthalein being used as indicator. Oxalic acid, fluorides and certain other impurities may be determined in the following manner : Ammonia and ammonium chloride are added to a measured volume of the sample and the mixture boiled. Any precipitate formed is filtered off and examined for iron and aluminium. The filtrate is boiled until the excess of ammonia has been expelled, a boiling solution of calcium chloride added and the mixture allowed to stand for twelve hours. The precipitate, which consists of calcium fluoride and calcium oxalate, is filtered off on a weighed Gooch crucible, and weighed. It is then washed into a flask, mixed with sulphuric acid and titrated with decinormal potassium permanganate in order to obtain the amount of oxalic acid or calcium oxalate, the fluoride being determined by difference.

Determination.—The strength of commercial solutions of hydrogen peroxide is expressed, generally, in terms of the volume of oxygen which they are capable

of yielding. The usual concentrations are 10 to 12 volumes, 20 volumes and 100 volumes. The relation between "volumes" and percentage of hydrogen peroxide by weight is as follows:

	Volume of Oxygen Liberated.	Percentage of Hydrogen Peroxide.
10 vols. hydrogen peroxide.	10 volumes.	3·04
20 vols. ,,	20 volumes.	6·08
100 vols. ,,	100 volumes.	30·40

The methods chiefly used in the determination of hydrogen peroxide are titration by means of decinormal potassium permanganate or iodine solution. The oxygen available for bleaching may also be determined directly with the aid of a nitrometer. The iodometric method is the more reliable of the titration processes, since it is not affected by the presence of oxidisable stabilising agents.

Titration with Iodine.—The sample is diluted with sufficient water to produce a "one volume" solution. A solution of 2 grms. of potassium iodide in 200 c.c. of water is mixed with 30 c.c. of sulphuric acid (1 in 2) and the mixture cooled, after which 10 c.c. of the diluted peroxide solution are run in and the flask allowed to stand for a short time to complete the reaction.

$$H_2O_2 + 2\,KI + H_2SO_4 = K_2SO_4 + 2\,H_2O + I_2.$$

The iodine liberated is determined by titration with decinormal sodium thiosulphate solution. Each cubic centimetre used is equivalent to 0·0017 grm. of hydrogen peroxide. It should be noted that when hydrogen peroxide acts upon potassium iodide in the absence of acid, the first reaction which takes place is

$$2\,KI + H_2O_2 = 2\,KOH + I_2.$$

The liberated iodine then reacts with the potassium hydroxide forming iodate and hypoiodite. These reactions are inhibited by the presence of sulphuric acid.

Titration with Potassium Permanganate.—This method depends upon the reaction

$$2\,KMnO_4 + 4\,H_2SO_4 + 5\,H_2O_2 = 2\,KHSO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2.$$

In making the determination, 10 c.c. of the diluted sample are pipetted into a beaker or flask and diluted to about 300 c.c. with water, after which 30 c.c. of 20 per cent. sulphuric acid are added. Decinormal potassium permanganate solution is then run in from a burette until a permanent faint pink colour is obtained. If the first few drops of permanganate added are not decolorised, or if a brownish coloration (due to undissolved oxides of manganese) is formed, more sulphuric acid should be added. Each cubic centimetre of decinormal potassium permanganate is equivalent to 0·0017 grm. of hydrogen peroxide. Such bodies as glycerol or salicylic acid affect the accuracy of the results, since they are oxidised simultaneously by potassium permanganate; M'Lachlan (*Proc. Chem. Soc.*, 1903, **19**, 216) considers that for such reasons as this, the permanganate method of titration is valueless. The presence of oxidisable bodies is indicated by a higher result being obtained with the permanganate method than by titration with iodine.

Measurement of the Volume of Oxygen Produced.—This determination, although rather troublesome, is in some respects more accurate than titration determination. The Sonnié-Moret method (*Rép. Pharm.*, 1899, II., 289) is as follows: 4 c.c. of the solution are introduced into a nitrometer containing mercury. A suspension of 0·4 grm. of finely ground manganese dioxide in 2 c.c. of a 15-20 per cent. solution of sodium hydroxide is then drawn into the nitrometer and mixed carefully with the peroxide. After completion of the reaction, and allowing the oxygen to cool, the level of the mercury in the two tubes is adjusted and the volume of gas read off and calculated to 0° C. and 760 mm. pressure by means of the formula

$$\frac{VP}{273 + t} = \frac{V'P'}{273 + t'}.$$

From the equation

$$MnO_2 + H_2O_2 = MnO + H_2O + O_2,$$

it is seen that one gramme-molecule of oxygen is liberated from 68 grms. of hydrogen peroxide. Hence 1 grm. of hydrogen peroxide will liberate $\frac{22,400}{68}$ c.c., *i.e.* 329·4 c.c., of oxygen at N.T.P.

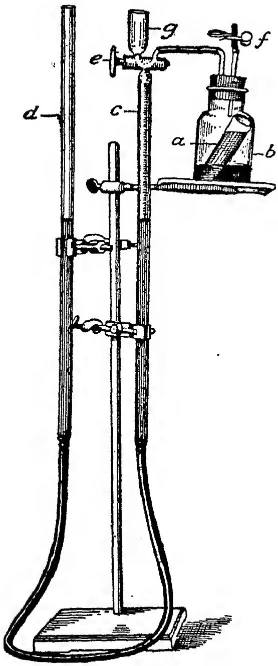


Fig. 37.—Nitrometer.

The following modification (see fig. 37) of the nitrometer method saves the use of mercury. The nitrometer is filled with brine which has been saturated with air, and connected by means of pressure tubing to a small decomposition bottle, in which are placed some potassium permanganate solution and dilute sulphuric acid. The peroxide solution (1 c.c.) is placed in the tube inside the bottle and the latter connected to the nitrometer as shown in the illustration. After standing for a short time to allow the system to attain atmospheric temperature, the three-way tap is opened carefully and the open tube of the nitrometer moved carefully until the level in both tubes is the same, *i.e.* until the air in the decomposition bottle and the nitrometer is at atmospheric pressure. The level of the liquid in the graduated tube is then read off. The decomposition bottle is now connected to the nitrometer by means of the three-way tap and the open tube is lowered to reduce the pressure. The bottle is then tilted to bring the peroxide in contact with the potassium permanganate and sulphuric acid. After the oxygen has been liberated and allowed to cool to atmospheric temperature, the open tube is again adjusted to atmospheric pressure and the volume of gas read off. The increase in volume is due to the oxygen liberated from the hydrogen peroxide. This is calculated to 0° C. and 760 mm. pressure. Since the gas in the tube is under the same pressure and temperature as the air was at the commencement of the determination, the volume of liberated oxygen (saturated with aqueous vapour) is equal to that of the brine displaced.

When it is necessary to calculate the results to "volumes," the nitrometer

method is useful, but titration methods are available also. Since 1 grm. of peroxide yields 329·4 c.c. of oxygen, each cubic centimetre of decinormal potassium permanganate is equivalent to 0·559 c.c.

It is convenient sometimes when controlling the strength of bleaching baths by titration tests to use a solution of potassium permanganate of such a strength that results by volume may be obtained directly without calculation. If a solution of potassium permanganate containing 5·655 grms. per litre be used, each cubic centimetre is equivalent to 1 c.c. of oxygen.

Titration by Means of Titanous Chloride.—Titanous chloride solution (*vide ibid.*) was recommended by Knecht for the titration of hydrogen peroxide. The sample is acidified with hydrochloric acid and titrated in an atmosphere of carbon dioxide. As the addition of the titanous chloride solution proceeds, the liquid first becomes yellow and then orange. After a maximum depth of colour has been produced, the colour fades gradually and at the end-point of the titration the solution becomes colourless. The hydrogen peroxide present is calculated from the equation

$$2\,TiCl_3 + H_2O_2 + 2\,HCl = 2\,TiCl_4 + 2\,H_2O.$$

Qualitative Tests for Hydrogen Peroxide.—In the absence of other bodies, such as nitrous acid, which decompose potassium iodide, the liberation of iodine from an acidified solution of this salt forms a simple test for the detection of hydrogen peroxide. The following tests are delicate and characteristic :

(1) *The Chromic Acid Reaction.*—A drop or two of potassium dichromate solution, some sulphuric acid and a little of the solution to be tested are placed in a test-tube. About 5 c.c. of ether are added, the tube closed and shaken. In the presence of hydrogen peroxide the ether will acquire a deep blue colour.

(2) *Knecht's Test.*—The reaction with titanous chloride solution noted above forms a delicate qualitative test for hydrogen peroxide. If a solution of titanous chloride be added to one containing hydrogen peroxide, a yellow or orange colour is produced so long as *excess* of hydrogen peroxide is present, but when the addition of titanous chloride is continued drop by drop the colour becomes gradually lighter and finally disappears.

Sodium Peroxide.

Commercial sodium peroxide is a yellowish powder which should contain from 95 to 98 per cent. of pure sodium peroxide, Na_2O_2, or 20·5 per cent. of "available" oxygen. Its equivalent in hydrogen peroxide may be calculated from the equation

$$Na_2O_2 + 2\,H_2O = 2\,NaOH + H_2O_2.$$

For the analysis of sodium peroxide a weighed quantity of the powder is first dissolved very carefully in an excess of dilute sulphuric acid. The powder must be added little by little, great care being taken to prevent it floating on the surface and to keep the mixture cooled. The solution obtained is tested in exactly the same way as hydrogen peroxide.

Sodium Perborate, $NaBO_3.4\,H_2O$.

Sodium perborate may be regarded as derived from the hypothetical perboric acid, HBO_3. It is a colourless crystalline compound which is sparingly soluble

in cold water (1·93 per cent. at 15° C.). Its aqueous solution contains hydrogen peroxide, borax and sodium hydroxide :

$$4\,NaBO_3 + 5\,H_2O = 4\,H_2O_2 + Na_2B_4O_7 + 2\,NaOH.$$

Each molecule of the crystalline salt, $NaBO_3.4\,H_2O$, yields one molecule of hydrogen peroxide, corresponding to 10·4 per cent. of available oxygen.

The analysis of sodium perborate is carried out in the same way as that of sodium peroxide.

Hypochlorous Acid and Chlorine.

Hypochlorous acid may be distinguished from a solution of chlorine by shaking the liquid with an excess of metallic mercury. When hypochlorous acid is present, a brownish-yellow precipitate of oxychloride of mercury, $HgO.HgCl_2$, is formed, whilst chlorine gives a white precipitate of mercurous chloride.

Determination of Hypochlorous Acid.—Taylor (*Bleaching Powder and Its Action in Bleaching*, p. 1) described a method for the determination of hypochlorous acid in the presence of chlorine based upon their different reactions with a solution of sodium arsenite. These reactions are represented by the equations

$$(1)\ As_2O_3 + 2\,Cl_2 + 2\,H_2O = As_2O_5 + 4\,HCl,$$
$$(2)\ As_2O_3 + 2\,HOCl = As_2O_5 + 2\,HCl.$$

Thus, for the same amount of arsenite oxidised, twice as much hydrochloric acid is produced when chlorine is the oxidising agent as in the case of hypochlorous acid. A measured volume of the solution to be tested is added to a known excess of decinormal sodium arsenite solution, and the mixture is made up to a definite volume. The unoxidised sodium arsenite is determined by titration with decinormal iodine solution, and the quantity of arsenious oxide which has been oxidised is calculated.

In another portion of the solution the *chloride* is determined by titration with decinormal silver solution. Taylor recommends the following method of titration : The solution is acidified with nitric acid, a little silver nitrate solution is added, the mixture boiled for about two minutes and a portion of it filtered. A little more silver nitrate solution is added to the filtrate, which is then returned to the remainder of the liquid and the whole boiled again. This operation is repeated until the filtered portion gives no further precipitate with silver nitrate. When the oxidising agent is pure chlorine, the amount of silver nitrate used (≡ amount of chloride present) is the same as the amount of arsenite oxidised. When hypochlorous acid is the oxidising agent, the chloride produced represents only half of the amount of arsenite oxidised. The following is an example :

	Arsenite Oxidised.	Chloride Produced.	Hypochlorous Acid, per cent.	Chlorine, per cent.
1	1·08	0·57	90	10
2	1·00	0·45	100	0
3	4·48	2·94	52	48
4	7·90	7·95	0	100

Treadwell (*Analytical Chemistry*, II., 655) gives a process based upon the action of potassium iodide. When potassium iodide is added to a solution of

hypochlorous acid acidified with hydrochloric acid the reaction which takes place is as shown in the equation

$$HOCl + HCl + 2\,KI = H_2O + 2\,KCl + I_2.$$

But when potassium iodide is added to chlorine-water the reaction is :

$$Cl_2 + 2\,KI = 2\,KCl + I_2.$$

A measured volume of decinormal hydrochloric acid is added to a solution of potassium iodide, followed by a known volume of the liquid to be tested. The liberated iodine is then determined by titration with sodium thiosulphate solution. The acidity of the titrated colourless liquid is then determined by titrating with decinormal sodium hydroxide in the presence of methyl orange. The potassium hydroxide produced by the reaction

$$HOCl + 2\,KI = KCl + KOH + I_2$$

requires half as much acid to neutralise it as is required of sodium thiosulphate solution to react with the iodine set free by the hypochlorous acid. Thus if

v c.c. of the mixture of chlorine and hypochlorous acid were taken,
t c.c. of $N/10$ hydrochloric acid were added,
T c.c. of $N/10$ thiosulphate solution were required by the iodine liberated,
and t_1 c.c. of $N/10$ alkali were required to neutralise the excess of acid,

then $(t - t_1)$ c.c. $N/10$ acid were required to neutralise the potassium hydroxide, and $2\,(t - t_1)$ c.c. $N/10$ thiosulphate solution were required to react with the iodine formed by the hypochlorous acid.

Hence $(t - t_1) \times 0{\cdot}005246 \quad$ = grms. HOCl in v c.c. of the solution,
and $T - 2\,(t - t_1) \times 0{\cdot}00355$ = grms. Cl in v c.c. of the solution.

A similar method (Klimenko, *Z. anal. Chem.*, 1903, **42,** 718) depends upon the fact that when potassium iodide reacts with hypochlorous acid in the absence of hydrochloric acid, only half as much iodine is liberated as when hydrochloric acid is present. Thus

$$HOCl + HCl + 2\,KI = H_2O + 2\,KCl + I_2,$$
$$2\,HOCl + 3\,KI = 2\,KCl + KOI + H_2O + I_2.$$

A measured volume of the solution is treated with an excess of a 0·5 N solution of potassium iodide and the liberated iodine determined by titration with sodium thiosulphate. The solution is then acidified with hydrochloric acid and the titration continued. The first reading gives the whole of the free chlorine and half of the hypochlorous acid, the second titration the remaining half of the hypochlorous acid present. If there is no further liberation of iodine on adding hydrochloric acid after completing the first titration, no hypochlorous acid is present.

Feigl and Schummer (*Z. anal. Chem.*, 1924, **64,** 249) proposed a method for the determination of hypochlorous acid in which an excess of a standard solution of antimony trichloride is added to a measured volume of the liquid acidified with hydrochloric acid, the excess of antimony chloride being determined by titration with a standard solution of sodium bromate, methyl orange or indigo

being used as indicator, both of which are immediately decolorised by free bromine. The reactions which take place are given by the equations

$$HOCl + SbCl_3 + HCl = H_2O + SbCl_5,$$
$$3\ SbCl_3 + NaBrO_3 + 6\ HCl = 3\ SbCl_5 + NaBr + 3\ H_2O,$$
$$NaBrO_3 + 5\ NaBr + 6\ HCl = 3\ Br_2 + 6\ NaCl + 3\ H_2O.$$

Bleaching Powder.

A good sample of bleaching powder should contain not less than 35 per cent. of "available" chlorine. It should be free from chlorates and iron, and dry and powdery in appearance, free from lumps.

When bleaching powder is extracted with water, the solution obtained is rather complex, containing calcium hypochlorite, calcium chloride, calcium hydroxide and hypochlorous acid. In addition, calcium chlorate, free chlorine and traces of iron and manganese may be present. The pink coloration which is sometimes seen in bleaching liquors is ascribed generally to the production of calcium permanganate, but Tarugi (*Gazz. Chim. Ital.*, 1905, **34**, 466) has shown that it can be obtained in the absence of manganese if iron be present, owing to the formation of calcium ferrate.

Determination of Moisture.—The moisture content of bleaching powder can be determined without loss of chlorine by drying a weighed sample at 50° C. under a pressure of 100 mm. At temperatures above 50° C. loss of chlorine occurs.

Determination of Total Chlorine.—A solution of the powder is made by grinding about 5 grms. to a paste with a little water, washing it into a 500 c.c. flask, and diluting with water. In Sutton's method of analysis a measured volume of the clear or filtered solution is treated with 25 c.c. of a solution of ferrous ammonium sulphate (40 grms. per litre) and excess of sulphuric acid. The mixture is heated to 100° C. and allowed to cool slightly. An excess of standard silver nitrate solution is then added and the mixture filtered. The precipitate is washed with water and the washings and filtrate titrated with decinormal potassium thiocyanate solution, in order to determine the unused silver nitrate. The ferrous ammonium sulphate is oxidised by the hypochlorite to ferric sulphate, chloride being simultaneously produced. When the total chlorine is known, and also the "available" chlorine, that present as *chloride* is obtained by difference.

Lunge (*Technical Chemist's Hand Book,* p. 194) gives a method based upon the use of sodium arsenite and silver nitrate in which the arsenite reacts in accordance with the equation

$$2\ Ca\ (OCl)\ Cl + As_2O_3 = As_2O_5 + 2\ CaCl_2.$$

Nakamura's modification is simpler and gives good results. The method depends upon the reduction of the hypochlorites present to chlorides by the action of hydrogen peroxide, in accordance with the equation

$$Ca\ (OCl)\ Cl + H_2O_2 = CaCl_2 + H_2O + O_2.$$

In carrying out the determination, a 0·5 per cent. solution is prepared by triturating 1 grm. of the sample with water and making up the mixture to 200 c.c. 50 c.c. of this solution, or an equal volume of bleach liquor if this is to be examined, is pipetted into a conical flask and 5 c.c. of a 3 per cent. solution of hydrogen peroxide then added. When the reaction ceases, the mixture is heated

slowly to the boiling point and boiled for several minutes to decompose the excess hydrogen peroxide. The mixture is then neutralised with dilute nitric acid, using phenolphthalein as indicator, and the *total chlorides* determined by titrating the liquid with a 0·1 *N* solution of silver nitrate. In this titration 1 to 2 drops of a solution of potassium chromate may be employed as indicator.

In determining the *total chlorides* by Nakamura's method, the residual material remaining from the determination of the available chlorine by Böttler's method (*vide infra*) may be employed.

Total chlorine may be determined also by boiling the solution with excess of ammonia, which converts hypochlorites into chlorides, which are then determined in the usual manner.

$$3\,Ca(OCl)_2 + 4\,NH_3 = 3\,CaCl_2 + 2\,N_2 + 6\,H_2O.$$

Determination of "Available" Chlorine.—The term "available chlorine" denotes all the chlorine that is capable of being liberated by an acid, and which is thus available for bleaching. The method commonly employed for its determination is based upon the power which chlorine has of liberating its equivalent of iodine from a solution of potassium iodide, this iodine then being determined by titration with decinormal sodium thiosulphate solution. About 10 grms. of the powder are weighed and extracted by triturating with water, the mixture being made up to 1 litre with distilled water. After shaking, and before the sediment has settled, 25 c.c. of the liquid are withdrawn by means of a pipette and placed in a stoppered bottle. About 1 grm. of potassium iodide and a slight excess of dilute sulphuric or hydrochloric acid are then added. The mixture is now titrated with decinormal sodium thiosulphate solution in the usual manner, each cubic centimetre used corresponding to 0·00355 grm. of chlorine.

Arsenious acid may be employed instead of sodium thiosulphate in the determination of "available" chlorine. A decinormal solution of sodium arsenite is run in to the bleaching powder solution from a burette until a drop of the liquid removed by means of a glass rod no longer turns iodised starch paper blue. A few drops of the starch-iodide solution used to impregnate the paper are then added to the liquid and the titration continued until the blue colour produced is finally discharged. Each cubic centimetre of decinormal arsenious acid solution used corresponds to 0·00355 grm. of chlorine. This titration may be simplified by using indigo carmine as the indicator, this body being decolorised by chlorine. In this case the operation is reversed. A measured volume of the arsenious acid solution and a little hydrochloric acid are placed in a flask together with a drop of the indigo carmine solution. The solution of bleaching powder is then run in from a burette until the colour is discharged or a faint yellowish tint produced.

Titration with sodium arsenite is carried out more quickly by Mohr's modification of the process, in which excess of sodium arsenite is added and the unoxidised portion determined by titration with decinormal iodine, but according to Griffen and Hedallen (*J.S.C.I.*, 1915, 530) the results obtained by this or by any other process of titration with arsenious oxide are about 0·6 per cent. below the true chlorine content.

Dienert and Wandenbulcke (*J. Text. Inst.*, 1923, A75) titrate with arsenious oxide solution in the presence of ammonium sulphate, which prevents the formation of iodates. Although both the iodometric and arsenious acid methods are equally accurate, the former is more convenient to carry out, but not accurate in the presence of ferric salts and chlorates.

Bleaching powder frequently contains traces of *ferric oxide*. When the sample is treated with hydrochloric acid or sulphuric acid, ferric salts are formed, which liberate iodine from potassium iodide. Similarly *chlorates* yield chlorine when treated with strong acids, which is co-estimated with that from the hypochlorites.

The action of ferric salts on potassium iodide may be prevented (Kedesky, *Mitt. K. Materialpruf*, 1914, **32**, 534) by the use of phosphoric acid or disodium hydrogen phosphate, which results in the formation of insoluble ferric phosphate. The liberation of chlorine from chlorates may be avoided also by substituting a weak acid such as phosphoric or acetic acid for hydrochloric acid.

Some other methods may be referred to briefly. Pontius (*Chem. Zeit.*, 1904, **28**, 59) treats the solution of the bleaching powder with sodium bicarbonate, adds a drop of starch solution and titrates the mixture with a decinormal solution of potassium iodide. The reactions which take place are in accordance with the equations

$$6\,Ca\,(OCl)\,Cl \rightleftharpoons 3\,CaCl_2 + 3\,Ca\,(OCl)_2,$$

$$3\,CaCl_2 + 3\,Ca\,(OCl)_2 + 6\,NaHCO_3 \rightleftharpoons 6\,CaCO_3 + 6\,NaCl + 6\,HOCl,$$

$$6\,HOCl + 6\,NaHCO_3 + 2\,KI \rightleftharpoons 2\,KIO_3 + 6\,NaCl + 6\,CO_2 + 6\,H_2O.$$

The end-point of the titration is the formation of a permanent light blue colour.

Kertesz (*Zeitsch. angew. Chem.*, 1923, **36**, 595) proposed the use of a decinormal solution of sodium nitrite in the presence of starch iodide as an indicator. The reactions are

$$NaNO_2 + HOCl = NaNO_3 + HCl,$$

$$NaNO_2 + Ca\,(OCl)\,Cl = NaNO_3 + CaCl_2.$$

Roberts and Roncali, and later Williams (*Chem. News*, 1913, **107**, 109), based a method upon the action of hypochlorites on hydrazine sulphate, whilst Ehrenfried (*The Melliand*, U.S.A., 1929, **1**, 763) proposed the use of a decinormal solution of potassium bromate with methyl orange as indicator. A known excess of decinormal sodium arsenite solution is added to the hypochlorite liquor, a few drops of methyl orange introduced, and some hydrochloric acid. The hypochlorite reacts with the arsenious acid in accordance with the equation given on p. 120. The mixture is then titrated with the bromate solution until the colour of the methyl orange is just discharged. So long as sodium arsenite is present it will react with the bromate in accordance with the equation

$$6\,Na_3AsO_3 + 2\,KBrO_3 + 2\,HCl = 2\,KCl + 2\,HBr + 6\,Na_3AsO_4.$$

When all the arsenite has been oxidised the next drop of bromate will cause the liberation of free bromine, which will destroy the red colour of the methyl orange :

$$KBrO_3 + 5\,HBr + HCl = KCl + 3\,H_2O + 3\,Br_2.$$

Determination of Chlorine by Volume.—A method for determining the "available" chlorine in bleach liquors, which can be completed in 40-50 seconds, consists of measuring the pressure exerted by the oxygen liberated by the action of hydrogen peroxide on the hypochlorites present. 10 c.c. of the liquor are pipetted into the bottle A, fig. 38, and 10 c.c. of hydrogen peroxide are introduced in the test-tube B. The stopper, carrying a connection to the manometer C, is then inserted tightly into the neck of the bottle and the zero of the mercury in the manometer is read off on the scale. The bottle is then tipped over until the hydrogen peroxide is emptied from the test-tube, and

the reaction allowed to proceed. The scale, which may consist of a piece of graph paper pasted on to a smooth board, may be calibrated from bleach liquors containing known amounts of "available chlorine" as determined by other methods, and the results expressed in terms of 35 per cent. bleach per gallon, or in such other units as may be desirable.

Böttler's Method of determining the "available" chlorine is similar to the foregoing, but the reaction bottle is connected to a nitrometer and the volume of oxygen produced by the action of the hydrogen peroxide on the bleaching powder solution is determined, from which the "chlorometric degree" of the material is easily calculated. The "chlorometric degree" of a bleaching liquor is the volume of available chlorine in litres, measured at N.T.P., present in 1 litre of the liquor, or in the case of the solid material, it refers to 1 kilo of the bleaching powder. For example, if a sample of bleaching powder is said to have a "chlorometric strength" of 105°, it means that 1 kilo of the material gives 105 litres of chlorine measured at N.T.P., or, since 1 gramme-molecule of chlorine occupies 22·4 litres, at N.T.P., a "chlorometric strength" of 105° will correspond to

$$\frac{70{\cdot}9}{22{\cdot}4} \times 105 \text{ grms. chlorine per kilo.}$$

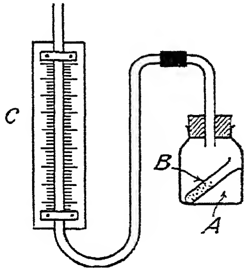


Fig. 38.—Apparatus for Rapid Determination of Chlorine by Volume.

Determination of Alkalinity.—For the estimation of the alkalinity of bleaching powder solutions the method of Orton and Jones (*Analyst*, 1909, **34**, 317) gives good results: A known volume of 0·1 *N* hydrochloric acid, in excess of the amount of the bleaching powder solution upon which the determination is to be made, is pipetted into a Drechsel bubbler and a known volume of the bleaching powder solution is then run in. A fairly rapid stream of air, freed from dust by first passing it through an air filter, is then drawn through the liquid in the bubbler, which is carefully shielded from light during this operation. After about 45 minutes' aeration, the liquid should be free from chlorine. This may be confirmed by the addition of one drop of a 0·1 per cent. solution of methyl orange; if any chlorine remains the indicator will be bleached and the aeration must be continued until the liquid remains sensibly reddish on the addition of a drop of the indicator. The acidity of the aerated liquid is then determined by titration with 0·1 *N* sodium carbonate.

In the case of solid basic hypochlorites (or compounds of calcium chloride and hypochlorite), the procedure is identical except that it will be found more convenient to introduce the sample into the bubbler previous to the addition of the acid.

The alkalinity of the sample is calculated from the following equations:

$$(1)\ Ca(OCl)_2 + 4\,HCl = CaCl_2 + 2\,H_2O + 2\,Cl_2,$$
$$(2)\ Ca(OH)_2 + 2\,HCl = CaCl_2 + 2\,H_2O.$$

The chlorine liberated according to (1) is that removed by the air stream. The thiosulphate or arsenite titre (0·1 *N*) of the bleaching solution will give the volume of 0·1 *N* hydrochloric acid reacting with the hypochlorite from the direct reading. The difference, then, between this latter value and that obtained

by titration with the 0·1 *N* solution of sodium carbonate will be equivalent to the volume of 0·1 *N* hydrochloric acid which has combined with the calcium hydroxide.

The method of Blattner (*Bull. Soc. chim.*, 1891, **1**, 116) is used commonly. It is based upon the fact that alkaline solutions of bleaching powder turn phenolphthalein pink, and may be titrated with decinormal acid until the pink colour is discharged. This change is not brought about by excess of acid, but by chlorine liberated by the action of the acid upon calcium hypochlorite. Owing to the hydrolysis of hypochlorites, decolorising of the indicator tends to take place before the alkali is completely neutralised and tends to lead to an estimate of the latter which is below the actual value.

Alkalinity may be determined also by adding a carefully neutralised solution of hydrogen peroxide to a measured volume of the bleaching powder solution until no more oxygen is given off. Methyl orange is then added and the alkalinity titrated with decinormal acid. If the methyl orange is bleached, it indicates that insufficient hydrogen peroxide has been added.

Chlorides.—The " available " chlorine is determined in one portion of the solution. Another portion is treated with a slight excess of hydrogen peroxide, boiled and cooled. The hypochlorites will now be present as chlorides :

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

The *total chlorine* is now determined by titration with silver nitrate solution and the chlorine as chloride obtained by difference.

Chlorates.—*Rupp's Method* for the estimation of chlorates and hypochlorites in the presence of one another (*Zeitsch. anal. Chem.*, 1917, **56**, 580) consists in pipetting into a stoppered litre bottle or flask a quantity of the liquor containing about 0·5 grm. of the two salts and diluting if necessary to about 100 c.c. 2 grms. of potassium iodide are added and dissolved in the liquor, which is then slightly acidified with acetic acid. The mixture is allowed to stand for 5 minutes and the iodine liberated by the hypochlorite or hypochlorous acid determined by titration with a 0·1 *N* solution of sodium thiosulphate. The *hypochlorite* present is calculated from the equation

$$HOCl + 2\,KI = KCl + KOH + I_2.$$

The chlorate present is determined from another portion of the sample to which 1 grm. of potassium iodide is added, followed by the addition of 30 c.c. of concentrated hydrochloric acid. After standing for 5 minutes 15 c.c. of a 1 per cent. solution of potassium iodide are added, the mixture well shaken, and the liberated iodine titrated with 0·1 *N* sodium thiosulphate solution. The difference between the two titrations gives the amount of *chlorate* present.

Carnot's Method (*Compt. Rend.*, 1896, **122**, 449) for the analysis of mixtures of chlorides, hypochlorites and chlorates consists of reducing the *hypochlorite* in alkaline solution with sodium arsenite, which will have no reducing action under these conditions on the chlorates present :

$$Na_3AsO_3 + HOCl = Na_3AsO_4 + HCl.$$

The *chlorates* are then reduced by means of a ferrous salt and the *total chlorine* determined finally by titration with silver nitrate. The determination of the three radicles may therefore be carried out in the same solution.

An accurately measured volume of the liquor is neutralised or made very slightly alkaline and then titrated with a 0·1 N solution of sodium arsenite, the end-point being determined by testing a drop of the liquid with a solution of potassium iodide and starch. The titration is finished when the addition of a drop of the sodium arsenite solution to the titrated solution destroys the blue colour of the starch-iodide solution. The liquid, which now contains only chlorides and chlorates, is acidified with a little sulphuric acid and heated for several minutes on a steam bath with a large excess of ferrous ammonium sulphate (about 20 times as much as the quantity of chlorate suspected). 20 c.c. of a 35 per cent. solution of sulphuric acid are then added, drop by drop. The air is displaced from the flask by a current of carbon dioxide and the flask stoppered with a rubber bung carrying a Bunsen valve. The flask and contents are then heated on a water-bath for 15-20 minutes. The following reaction takes place:

$$HClO_3+6(NH_4)_2SO_4.FeSO_4+3H_2SO_4=3Fe_2(SO_4)_3+6(NH_4)_2SO_4+HCl+3H_2O.$$

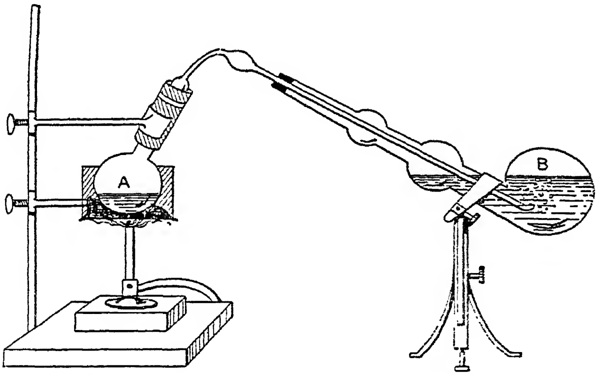


Fig. 39.—Apparatus for Determination of Chlorine.

On cooling, the solution is diluted and 10 c.c. of a solution added prepared by dissolving 67 grms. of crystallised manganous sulphate in 500-600 c.c. of water to which 138 c.c. of phosphoric acid (sp. gr. 1·7) and 130 c.c. of sulphuric acid (sp. gr. 1·82) have been added, the mixture being made up to 1 litre (Treadwell, *Analytical Chemistry*, II, 607). The excess ferrous salt is then determined by titration with a 0·1 N solution of potassium permanganate and the amount of chlorate calculated from the foregoing equation, or

$$ClO_3' + 6\,Fe^{\cdot\cdot} \rightleftarrows 6\,Fe^{\cdot\cdot\cdot} + Cl'.$$

The solution, which now contains all the chlorine as chloride, is decolorised by the addition of a drop of a dilute solution of ferrous sulphate and the total chlorine determined by the addition of an excess of a 0·1 N solution of silver nitrate, titrating back the excess with ammonium thiocyanate. The end-point is denoted by the formation of red ferric thiocyanate.

De Keghel (*Les Produits de Blanchiment,* p. 79) gives the following method of analysis, the apparatus used being shown in fig. 39. When chlorates are

heated with hydrochloric acid, chlorine is evolved in accordance with the equations

$$Ca\,(ClO_3)_2 + 2\,HCl = CaCl_2 + 2\,HClO_3,$$
$$2\,HClO_3 + 10\,HCl = 6\,H_2O + 6\,Cl_2.$$

Hypochlorites are decomposed also, but the chlorine produced from them can be determined separately and allowed for. Hence, if a known weight of bleaching powder, or a definite volume of its solution, be heated with excess of hydrochloric acid and the chlorine produced passed into a solution of potassium iodide, the total chlorine due to hypochlorites and chlorates may be determined by titration. In de Keghel's method, 25 c.c. of the solution and a small piece of magnesite are placed in the flask A, and in the retort B sufficient dilute potassium iodide solution to cover the end of the delivery tube from the flask. Hydrochloric acid is then added to the contents of the flask and the mixture heated until the chlorine has been expelled. The retort B should be immersed in cold water during the distillation. Its contents are washed into a flask and the liberated iodine determined by titration with decinormal sodium thiosulphate solution.

Methods of Expressing "Available" Chlorine in Bleaching Solutions.—The strength of a bleaching solution may be expressed in terms of:

(1) The Twaddell hydrometer scale.
(2) Grammes of "available" chlorine per litre.
(3) Litres of chlorine gas per litre of liquor, or "chlorometric degrees."

Hydrometer readings naturally are only approximate, but they are used frequently on account of the extra time required for titration. Moreover a practical bleacher often understands the significance of degrees Twaddell better than a chemical method of expression. When using a titration method the burette may be graduated to give direct readings in degrees Twaddell or grammes per litre.

The quickest method of titration is that in which the standard solution used is placed in a beaker or flask together with an indicator, as in the arsenious acid process, and the bleaching solution run in from a burette. For direct readings in grammes per litre the burette must be graduated in accordance with the equation

$$\frac{\text{c.c. of decinormal solution} \times 1000}{\text{c.c. of bleaching solution}} = \text{grammes per litre.}$$

When the scale is specially graduated, it is of course necessary to place in the beaker the exact number of cubic centimetres of the decinormal solution for which the scale is made. If the decinormal solution is run into the bleaching liquor, the readings of an ordinary burette may be made to represent grammes per litre by placing in the beaker that number of cubic centimetres of the bleaching liquor which fulfils the condition

$$\frac{1\text{ c.c. } N/10 \text{ solution} \times 0{\cdot}00355 \times 1000}{x \text{ c.c. bleaching solution}} = 1 \text{ grm. per litre,}$$

$$i.e.,\ x = 3{\cdot}55.$$

The relation between degrees Twaddell, specific gravity, grammes per litre and "chlorometric degrees" is given in the following table :

° Tw.	Sp. Gr.	"Grammes per Litre."	"Chlorometric Degree."
0·5	1·0025	1·40	0·45
1·0	1·0050	2·71	0·86
2	1·0100	5·58	1·77
3	1·0150	8·41	2·67
4	1·0200	11·41	3·63
5	1·0250	14·47	4·61
6	1·0300	17·36	5·51
7	1·0350	20·44	6·5
8	1·0400	23·75	7·5
9	1·0450	26·62	8·3
10	1·0500	29·60	9·4
15	1·0750	45·70	14·5
20	1·1000	61·50	19·6
0·3	1·0015	1	0·32
0·72	1·0036	2	0·64
1·1	1·0055	3	0·96
1·5	1·0075	4	1·27
1·8	1·0090	5	1·59
2·2	1·0110	6	1·91
2·5	1·0125	7	2·23
2·9	1·0145	8	2·55
3·1	1·0155	8·5	2·70

CHAPTER X.

WATER AND EFFLUENTS.

WATER.

In the analysis of water for industrial purposes the determinations made depend upon the use to which the water is to be put. Organic purity may be of less importance than the quantity and nature of the salts present. Often the chief consideration is the hardness, whilst in the case of water used for steam raising, the proportion of alkali salts is of considerable importance.

The organic purity of a water is determined, chiefly, by the ammonium salts and nitrogenous compounds which yield ammonia when distilled with an alkaline solution of potassium permanganate, which are present. The information thus gained is supplemented by the determination of the oxygen which the water absorbs from potassium permanganate and the proportions of chlorides, nitrites or nitrates present. It should be noted that the results of the analysis of water are expressed sometimes as grains per gallon and sometimes as parts per 100,000.

Determination of Ammonia.

The ammonia in water occurs in two forms, (*a*) saline or free ammonia, (*b*) protein or "albuminoid" ammonia which is evolved when the water is boiled with a solution of sodium hydroxide containing potassium permanganate.

The quantity of ammonia present in water is never sufficient to determine by titration, and a colorimetric method of estimation is always employed, depending upon the fact that very small amounts of ammonia produce a brownish-coloured compound with Nessler reagent, a solution of double iodide of mercury and potassium ($HgI_2.2\,KI$) in sodium hydroxide.

The following solutions are required:

(1) *Nessler Solution.*—35 grms. of potassium iodide, 13 grms. of mercuric chloride and about 800 c.c. of water are boiled together and stirred until solution is obtained. The solution is cooled and a cold saturated solution of mercuric chloride in water is added little by little until the red periodide of mercury which is formed just begins to be permanent. 120 grms. of sodium hydroxide are then added and the solution diluted to one litre. A little more mercuric chloride solution is added and the precipitate formed allowed to settle. Nessler solution should be slightly yellow in colour; if not so, more mercuric chloride solution must be added.

(2) *Alkaline Permanganate Solution.*—8 grms. of potassium permanganate are dissolved in about 250 c.c. of water in a flask of about two litres capacity; 120 grms. of sodium hydroxide are dissolved separately in water, the solution added to the permanganate solution and the whole diluted to about 1·5 litres with water. The contents of the flask are now boiled gently until about 500 c.c. have been evaporated. The residue will now be free from ammonia, and after cooling is poured into a stock bottle.

(3) *Standard Ammonia Solution.*—3·141 grms. of pure ammonium chloride are dissolved in ammonia-free water and the solution made up to one litre. Each cubic centimetre contains 0·001 grm. of ammonia. The solution is diluted to one-hundredth of this concentration before use.

(4) *Ammonia-free Distilled Water.*—A little sodium carbonate is added to ordinary distilled water or tap water, after which the water is re-distilled, the distillate being rejected until 50 c.c. give no coloration with Nessler solution.

Determination of Saline and "Albuminoid" Ammonia.—A distilling flask of about one litre capacity is connected to a vertical worm condenser. About 500 c.c. of tap water are placed in the flask and boiled and 100 c.c. of distillate collected. This is to ensure freedom of the apparatus from ammonia. The flask is then emptied and 500 c.c. of the water to be tested are introduced. A little pure sodium carbonate is added and 100 c.c. of the water are then distilled off. This distillate is well mixed and 50 c.c. of it are treated in a Nessler cylinder with 2 c.c. of Nessler solution. After about 3 minutes the colour is matched with that given by the diluted standard ammonia solution. A measured volume of this solution is placed in a second cylinder, diluted to 50 c.c. with ammonia-free water and 2 c.c. of Nessler solution added. After 3 minutes the colour is compared with that of the first mixture, and if the colours do not match, further mixtures are made up and tested until the two tints are identical. Since the quantity of ammonia required to match the colour given by 50 c.c. of the distillate is known, that present in the 500 c.c. of water taken can be calculated.

Much trouble can be saved by using a Lovibond tintometer and a special series of glasses standardised in terms of ammonia.

After distilling off the free and saline ammonia, 50 c.c. of the alkaline permanganate solution are poured into the distilling flask and another 100 c.c. of water distilled off and tinted in the same manner. This gives the "albuminoid ammonia" derived from organic matter capable of being decomposed by potassium permanganate in the presence of alkali.

An organically-pure water should contain only traces of either saline or albuminoid ammonia. A few examples are given in the following table.

	Saline Ammonia per 100,000 parts.	Albuminoid Ammonia
Water of high purity, .	0·005	0·005
Good sewage effluent, .	0·05 to 0·10	0·05 to 0·06
Sewage, . . .	2 to 4	1 to 2

Determination of Oxygen Absorbed from Potassium Permanganate.

In this test potassium permanganate is used in the presence of sulphuric acid, oxygen being given up in accordance with the equation

$$2\,KMnO_4 + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O.$$

The oxygen which disappears is a measure of the total oxidisable matter present in the water, whether nitrogenous or not. In order to obtain comparable results, the test must be carried out under standardised conditions, since the temperature, time of action and other factors affect the results. The following method is employed: Two stoppered bottles of about 250 c.c. capacity are cleaned with bichromate and sulphuric acid. In one of these a measured volume of the

water to be tested is placed (from 50 to 100 c.c., according to the purity) and in the other the same volume of freshly-distilled water, which must be quite free from organic matter. The bottles are placed in a water-bath maintained at a temperature of 80° F. and after a time 10 c.c. of a centinormal solution of potassium permanganate and 10 c.c. of dilute sulphuric acid (1 : 3) at 80° F. are added to each bottle. The bottles are allowed to stand in the water-bath at 80° F. for exactly four hours, more potassium permanganate being added if decolorisation takes place. Potassium iodide solution is now added and the liberated iodine determined by titration with centinormal sodium thiosulphate solution. The blank experiment gives the total oxygen present, and the difference between the two titrations represents the oxygen absorbed by the organic matter in the water. Each cubic centimetre of $N/100$ sodium thiosulphate solution represents 0·00008 grm. of oxygen. An unpolluted water should not absorb more than 0·10 part of oxygen per 100,000.

Determination of Nitrates and Nitrites.

There are many methods for the determination of nitrates in water, including (1) reduction to ammonia and estimation with Nessler solution, (2) the liberation and measurement of nitric oxide, (3) titration with indigo carmine solution, (4) colorimetric methods.

Of these methods **Sprengel's phenoldisulphonic acid method** is most commonly employed, although it is not very reliable when large amounts of chlorides are present. Phenoldisulphonic acid is prepared by mixing two parts of phenol with five parts of concentrated sulphuric acid and heating the mixture on a water-bath for about 8 hours, with occasional stirring. The mixture is cooled and 1·5 volumes of water and 0·5 volume of concentrated hydrochloric acid are added. A standard solution of potassium nitrate is also required, made by dissolving 0·722 grm. of the pure salt in 1 litre of water ; each cubic centimetre contains 0·0001 grm. of nitrogen as nitrate. The test is made in the following manner : 10 c.c. of the water are evaporated to dryness on a water-bath. The residue is mixed with 1 c.c. of the phenoldisulphonic acid reagent and heated on the water-bath for 15 minutes. At the same time 5 c.c. of the standard nitrate solution (0·0005 grm. N) are similarly treated. The residues are washed into a 100 c.c. graduated cylinder with distilled water, made alkaline with ammonia and diluted to 100 c.c. In general, the colour of the liquid in one cylinder will be darker than that of the other. The darker solution is now diluted with water until its tint is the same as that of the other solution and the proportion of nitrogen as nitrate is then calculated. Unpolluted water rarely contains more than 0·5 part of nitrogen as nitrate per 100,000.

The Pyrogallic Acid Method.—This method is useful for the approximate and rapid determination of the nitrates present in water or effluents. The following description is taken from *Methods of Chemical Analysis as Applied to Sewage and Effluents*, published by the Ministry of Health. 10 c.c. of the sample, filtered from all suspended solids, are poured into a test-tube of rather thick glass (a bacteriological test-tube 15 cm. × 1·25 cm.) and about 0·2 grm. of pyrogallic acid is dissolved in this and the solution made uniform by shaking. The pyrogallic acid can be measured with sufficient accuracy after a little practice. By means of a pipette with a bulb at the top and a fine orifice at the outlet, lowered to the bottom of the test-tube, 2 c.c. of concentrated nitrate-free sulphuric acid are allowed to flow slowly to the bottom of the tube so as to form a layer beneath the aqueous liquid. Before withdrawing the pipette the upper end must be closed, in order to prevent the acid remaining in it from

mixing with the upper layer. About 0·1 grm. of pure dry powdered sodium chloride (which need not be weighed) is then dropped into the tube. A purple band is formed at the junction of the two layers, the intensity of which is proportional to the nitrate present. Ardern and Crabtree add 1 c.c. of a 4 per cent. solution of pyrogallic acid. Standards for comparison are made with 0·1 to 0·6 part of nitrogen as nitrate per 100,000.

The Gladstone-Tribe Method.—In this method the nitrate is reduced to ammonia by means of a zinc-copper couple. The ammonia is then distilled off and determined with Nessler solution. The method is useful when much chloride is present, which affects the accuracy of the results given by the phenol-sulphonic acid process. It is important not to take more water than will correspond to about 15 c.c. of the standard dilute solution of ammonium chloride. Hence it is advisable to determine the nitrogen as nitrate approximately by the pyrogallic acid method. Free ammonia or saline ammonia must also be known and allowed for or removed by boiling the water. This is only necessary when much is present, as in the case of effluents. The method recommended by the Royal Commission on Sewage Disposal is to dilute from 10 to 25 c.c. of the liquid to 150 c.c. with distilled water, add 5 c.c. of calcium bicarbonate solution and concentrate the mixture to 20 c.c. in a round-bottomed resistance glass flask in a draught cupboard. The residue is cooled and diluted to 100 c.c. with distilled water. When only a little ammonia is present it can be determined in a blank experiment. The following reagents are required, in addition to the Nessler solution and standard ammonium chloride solution :

(1) A 3 per cent. solution of crystalline copper sulphate.
(2) Pure dry sodium chloride.
(3) A solution of calcium bicarbonate, prepared by saturating lime water with carbon dioxide.
(4) Pure zinc foil.

If the water contains not more than 0·2 part of ammoniacal nitrogen per 100,000, the following procedure is adopted : 10 c.c., filtered if necessary, are placed in a wide-mouthed stoppered bottle of about 100 c.c. capacity, 0·2 grm. of sodium chloride added and the bottle filled up to the shoulder with ammonia-free distilled water. The zinc-copper couple is added and the bottle kept over-night at a temperature of about 80° F. A second bottle is treated in exactly the same way, except that no zinc-copper couple is added. The contents of these bottles are washed into distilling flasks and the ammonia distilled off and determined by means of Nessler solution. The difference between the two gives the ammonia derived from the nitrites and nitrates.

The zinc-copper couple is made freshly each time. A strip of clean zinc foil (4 in. $\times$ $2\frac{3}{4}$ in.), rolled into a coil, is immersed in the copper sulphate solution until it is coated with copper. It is then washed, first with tap water and finally with distilled water. Neither the copper sulphate solution nor the couple should be used twice.

The Detection of Nitrites.—Nitrates, being the final products of the oxidation of nitrogenous organic matter, are not of great importance themselves, but their presence indicates that the water is being drawn from a source subject to pollution. The presence of nitrites would indicate comparatively recent pollution. They may be detected by the following tests :

When much nitrite is present a blue colour is produced when potassium iodide, starch and dilute sulphuric acid are added to the water. Other bodies such as hypochlorites act in the same way.

When even traces of nitrite are present, a brown colour due to Bismarck Brown is produced when the water is acidified slightly and a little metaphenylenediamine hydrochloride added.

The Griess-Illosvey test is very delicate: Two solutions are required, viz., (*a*) sulphanilic acid 0·5 grm., glacial acetic acid 30 c.c., water 120 c.c., (*b*) α-naphthylamine hydrochloride 0·2 grm., dissolved in 20 c.c. of glacial acetic acid by the aid of heat, the clear solution being poured off and diluted to 150 c.c. with 20 per cent. acetic acid. 2 c.c. of (*a*) and of (*b*) are added to the solution to be tested and the mixture warmed to 80° C. for about 10 minutes. A pink colour is produced in the presence of nitrites. For quantitative results the colour may be matched with that obtained with a standard solution of potassium nitrite. This standard solution is prepared by dissolving a weighed quantity of silver nitrite in water, precipitating the silver with potassium chloride, filtering off the silver chloride and diluting the filtrate to a definite volume.

The Determination of Chlorides.

Chlorides are determined by titration with decinormal silver nitrate solution, potassium chromate being used as indicator. The results are returned as *chlorine*, since the base is not necessarily known. When the water contains sodium carbonate, it must be neutralised exactly with very dilute acetic acid (*e.g.*, centinormal) before titration.

Determination of Dissolved Solids and Suspended Matter.

Dissolved solids are determined by evaporating a measured volume of the water to dryness in a weighed dish and drying the residue to constant weight. The volume of water to be taken depends upon the proportion of solids present, but in most cases 100 c.c. are sufficient. In order to determine suspended matter, the sample is shaken well and about 250 c.c. decanted off rapidly before the sediment has settled. This is filtered through a weighed Gooch crucible, the residue dried and weighed.

The Determination of Hardness.

The total hardness of a water can be determined quickly by means of a standard soap solution, but when accurate results are required, or both temporary and permanent hardness have to be determined, more exact methods of analysis must be employed.

The Determination of Hardness by Means of Soap Solution.—This depends upon the reaction

$$2\,C_{17}H_{33}COOK + CaCO_3 = (C_{17}H_{33}COO)_2Ca + K_2CO_3.$$

Thus 2×282 grammes of oleic acid are equivalent to 100 parts of hardness expressed as calcium carbonate. Hence, a solution of potassium oleate containing 5·64 grms. of oleic acid per litre would precipitate $\frac{100 \times 5{\cdot}64}{2 \times 282}$ grms. of calcium carbonate, *i.e.*, 1 grm. Each cubic centimetre of this solution would correspond to 0·001 grm. of hardness expressed as calcium carbonate. Since considerable quantities of soap solution are used in the routine testing of softened

water, it is convenient to prepare a stock solution which can be diluted and standardised as required.

Preparation of Stock Solution.—About 57 grms. of oleic acid are dissolved in 300 c.c. of industrial spirit and carefully neutralised to phenolphthalein by stirring in a concentrated solution of potassium hydroxide, the pink colour finally being discharged by the addition of a little oleic acid. The solution is diluted to 1 litre with a mixture of 2 volumes of spirit to 1 volume of distilled water. The standard solution is made by diluting 100 c.c. of the stock solution to 1 litre with industrial alcohol and water (2 : 1) and, after allowing the solution to stand for some hours, filtering off any insoluble residue.

Standardisation of Soap Solution.—A standard solution of calcium chloride is prepared in the following manner: 1 grm. of Iceland spar or pure calcium carbonate is dissolved in dilute hydrochloric acid. The solution is evaporated to dryness on a water-bath, the residue dissolved in water, re-evaporating to expel the last traces of hydrochloric acid. The calcium chloride is then dissolved in water and the solution diluted to one litre. In order to standardise the soap solution, 10 c.c. of the calcium chloride solution are pipetted into a stoppered bottle of about 150 c.c. capacity and 40 c.c. of distilled water are added. The soap solution is run in to the bottle from a burette, at first about one cubic centimetre each time, the stopper being replaced after each addition and the contents of the bottle well shaken. When the first indications of a foam or lather are observed, the soap solution is added cautiously, a few drops at a time. After each addition the bottle, after shaking, is laid on its side and the lather is observed carefully. If it disappears rapidly, more soap solution is required. The end-point of the titration is the formation of a foam or lather which remains for at least one minute when the bottle is laid on its side. Since 10 c.c. of the standard calcium chloride solution correspond to 0·01 grm. of calcium carbonate, the value of the soap solution in terms of calcium carbonate can be calculated easily.

Soap solution is used, generally, to determine *total hardness* only. In order to obtain consistent results, certain points must be noted, viz. : (1) the volume of water tested must always be the same; (2) when more than 10 c.c. of the soap solution are required to produce a lather, the results become inaccurate owing to the interference of insoluble calcium and magnesium soaps. When the total hardness of a water is unknown, a trial experiment is made with 50 c.c., the soap solution being run in fairly rapidly. From the volume used, a suitable dilution of the water may be made so that about 10 c.c. of soap solution will be required for 50 cubic centimetres of water.

Permanent hardness may be determined as follows: A measured volume of the water, 100 c.c., is boiled gently for about 45 minutes, cooled, and made up to the original volume with cold carbon dioxide-free water. After mixing well, the precipitated temporary hardness is allowed to settle or removed by filtration and the permanent hardness in the filtrate determined as described above. The temporary hardness is obtained by difference.

Other methods depending on the use of standard soap solutions have been proposed. That of Winkler (*Zeitsch. anal. Chem.*, 1914, 409) may be quoted as an example: The water is titrated with $N/10$ hydrochloric acid in the presence of methyl orange until the neutral tint is produced, and the colour destroyed by a drop of bromine water. Phenolphthalein is now added and then $N/10$ sodium hydroxide until the colour becomes pink. This pink colour is just discharged with $N/10$ hydrochloric acid, after which an additional 0·1 c.c. of the acid is added and the solution titrated with a standard solution of sodium palmitate, the end-point being the production of a pink colour; it is better,

however, to take a distinct red as the end-point and deduct 0·3 c.c. from the reading. The volume of hydrochloric acid used gives the *temporary hardness* (1 c.c. acid is equivalent to 0·005 grm. $CaCO_3$), and from the volume of palmitate solution used the *total hardness* may be calculated.

$$2\,C_{15}H_{31}COONa + CaCl_2 = (C_{15}H_{31}COO)_2Ca + 2\,NaCl,$$
$$C_{15}H_{31}COONa + H_2O = C_{15}H_{31}COOH + NaOH.$$

The standard palmitate solution is made by dissolving 25·6 grms. of pure palmitic acid in a mixture of spirit and water and neutralising the solution with alcoholic sodium hydroxide solution. After diluting to a litre, the solution is standardised with 50 c.c. of saturated lime water which has been accurately neutralised with N/10 hydrochloric acid.

Hehner's Method.—The use of soap solution is now confined practically to the examination of softened water. For other purposes either Hehner's method or one of its modifications is employed. This method depends upon the neutralisation of bicarbonates with hydrochloric or sulphuric acid, using methyl orange as indicator, and the decomposition of " permanent hardness " by means of sodium carbonate :

$$Ca\,(HCO_3)_2 + 2\,HCl = CaCl_2 + 2\,CO_2 + 2\,H_2O,$$
$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

Temporary Hardness.—In Hehner's original method 100 c.c. of the water are titrated with decinormal hydrochloric acid, methyl orange being used as indicator. Each cubic centimetre of acid used corresponds to 0·005 grm. of " temporary hardness." The accuracy of the determination depends upon the degree of insensibility of methyl orange to carbonic acid. Whilst in dilute solutions carbonic acid does not affect methyl orange, yet if present in considerable quantities the acid has a distinct action, and tends to obscure the end-point. Proctor (*J.S.C.I.*, Jan., 1904) suggested carrying out a blank experiment side by side with the water under examination. Pfeifer and Wartha (*loc. cit.*) overcome the difficulty by using alizarin as the indicator. The water is placed in a porcelain dish, a drop of the indicator added and the acid run in until the violet colour changes to a distinct lemon yellow. The water is now boiled to expel carbon dioxide, when the violet colour returns. This is destroyed by adding another drop of acid, the operation being repeated until the violet colour no longer returns.

Newlands (*J.S.C.I.*, 1916, 445) prefers methyl red to methyl orange since it has a sharper colour change (yellow to red), and the end-point is at $pH = 5$ instead of $pH = 4$ in the case of methyl orange. Its use offers no advantage over that of alizarin since it is sensitive to carbon dioxide and titration must be carried out therefore at the boiling point.

The real difficulty connected with the use of methyl orange is the indefinite colour change, which is particularly noticeable in artificial light. Bromophenol blue is free from this disadvantage. It changes from yellow to bluish-purple between $pH = 2{\cdot}8$ and $4{\cdot}6$, and the colour change is most marked at $pH = 3{\cdot}8$, which corresponds to the neutral tint of methyl orange. Atkin and Gardner (*J.L.T.C.*, 1923, 87) recommend the use of bromophenol blue, for the foregoing reasons, in the determination of temporary hardness. Burton and Haslam (*J.S.C.I.*, 1927, 111 T) give the following method of working : First, a blank experiment is made with 200 c.c. of distilled water and the indicator, the volume of decinormal acid required to produce the colour change being deducted from that used when titrating the water. For accurate work it is desirable to titrate

to the same pH value by using a comparator and a solution of approximately $pH = 3{\cdot}7$, made by taking a decinormal solution of formic acid and adding half the quantity of sodium hydroxide solution which would be required to neutralise it. In the determination of temporary hardness 200 c.c. of the water are titrated to $pH = 3{\cdot}7$, the volume of acid required in the blank experiment deducted, and the remainder calculated to calcium carbonate in the usual manner.

Permanent Hardness.—In Hehner's original method, 100 c.c. of the water are evaporated to dryness on a water-bath with a known volume of decinormal sodium carbonate solution, which should contain about twice as much sodium carbonate as that required to precipitate the "permanent hardness." The residue is extracted with freshly boiled hot distilled water, the mixture filtered, the filter washed four times with hot distilled water, the filtrate and washings cooled and titrated with decinormal hydrochloric acid in the presence of methyl orange. Each cubic centimetre of decinormal carbonate solution which has disappeared corresponds to 0·005 grm. of permanent hardness expressed as calcium carbonate.

If only a little sodium carbonate remains, the results cannot be relied on and it is better to repeat the experiment using a larger volume of decinormal sodium carbonate solution. The results are unreliable; also, when an alkali carbonate is present. Calcium carbonate is soluble in water to the extent of 2·7 parts per 100,000, and magnesium carbonate is still more soluble. When much "magnesium hardness" is present, the results given by Hehner's method are too high.

Pfeifer and Wartha (*loc. cit.*) proposed using a mixture of equal volumes of sodium carbonate and sodium hydroxide in order to convert the magnesium into magnesium hydroxide, which only dissolves to the extent of 0·9 part per 100,000; but in this case filtration introduces a fresh source of error, since cellulose adsorbs sodium hydroxide. If, however, filtration be dispensed with, good results are obtained. The water (200 c.c.) is boiled for about 15 minutes in a hard glass flask, to expel carbon dioxide, 50 c.c. of a mixture of equal volumes of decinormal sodium hydroxide and sodium carbonate solutions are then added and the mixture concentrated to about 70 c.c. The mixture is then cooled, washed into a 100 c.c. flask or stoppered cylinder with carbon dioxide-free water, shaken and allowed to stand for a short time; 50 c.c. of the clear solution are then removed by means of a pipette and titrated.

Burton and Haslam (*loc. cit.*) found that when a Munktell No. 1 F 18·5 cm. filter paper was used there was extremely little difference in the results obtained by filtration and sedimentation, and that they were the same when either methyl orange or bromophenol blue was used as indicator.

Total Hardness.—When only a small quantity of water is available, the total hardness can be determined with accuracy in the following way: 100 c.c. of the water are made faintly acid with hydrochloric acid and concentrated to about 25 c.c. This residue is cooled and neutralised carefully with decinormal alkali. A measured volume of decinormal sodium carbonate solution is then added and the experiment completed as in the determination of permanent hardness. If the water be titrated with acid before concentration and the temporary hardness thus determined, the permanent hardness is given by difference.

"**Magnesium Hardness.**"—In order to calculate the quantities of lime and sodium carbonate necessary to soften water, the "magnesium hardness" must be known, since each part will require two equivalents of lime, the second to convert magnesium carbonate into magnesium hydroxide.

Pfeifer and Wartha Method.—A measured volume of the water (*e.g.*, 100 c.c.) is exactly neutralised with decinormal hydrochloric acid in the presence of alizarin and washed into a 250 c.c. flask by means of carbon dioxide-free water. 50 c.c. of lime water are added and the mixture diluted to 255 c.c. with boiling distilled water. The flask is closed, shaken and allowed to stand until the contents are cold. An aliquot part of the clear liquid (50 c.c.) is then removed by a pipette and titrated with decinormal hydrochloric acid, phenolphthalein being used as indicator. The strength of the lime water is found also by a separate titration. The reaction is,

$$MgCl_2 + Ca\,(OH)_2 = Mg\,(OH)_2 + CaCl_2.$$

The calculation is illustrated by the following example :

50 c.c. lime water required 22·0 c.c. *N*/10 acid,
50 c.c. mixture ,, 21·5 ,, .

Hence (22·0 — 21·5) c.c. *N*/10 acid is equivalent to the " magnesium hardness " in the 50 c.c. titrated, and 5 × 0·5 c.c. gives that of the 100 c.c. of water taken. The magnesium hardness is expressed generally in terms of calcium carbonate (1 c.c. ≡ 0·005 grm. $CaCO_3$), but if magnesia (MgO) be required, the factor is 0·002. When determining " magnesium hardness " by this method it is absolutely essential that at least half of the lime water should remain at the end of the experiment.

Method of Burton and Haslam.—The diminishing solubility of lime in water with increasing temperature may introduce an error. The solubility expressed as calcium oxide is 0·129 at 10° C. and 0·060 at 100° C. Thus, when a mixture of 100 c.c. of water and 100 c.c. of lime water is heated to 100° C., lime may actually be precipitated. The addition of the indicator at the commencement of the experiment is also undesirable. The following method, which avoids these difficulties, is a modification of the original method due to Atkin and Burton (*J.S.L.T.C.*, 1927, 294). If the temporary hardness has not been determined already, 200 c.c. of the water are titrated with *N*/10 hydrochloric acid in the presence of bromophenol blue as already described. The volume of acid used, after deducting that required by the blank experiment, is added to 200 c.c. of the water in a flask and the mixture boiled for 30 minutes to expel carbon dioxide and reduce the volume to about 70 c.c. After this, 50 c.c. of clear saturated lime water are added, the mixture heated to 100° C. in a water-bath, the flask closed with a rubber bung and its contents cooled. When cold the mixture is diluted to 200 c.c. with well boiled cold distilled water, again closed, shaken and allowed to stand overnight. 100 c.c. of the clear liquid are then removed and titrated with decinormal acid in the presence of bromophenol blue, 50 c.c. of the lime water being titrated also. Since each c.c. of *N*/10 acid corresponds to 0·005 grm. $CaCO_3$, the magnesium hardness is obtained by multiplying the difference between the two titrations by 2. The volume of water taken for the analysis must be such that the amount of lime water used up does not exceed 5 c.c.

Anderson's Method.—In this method the magnesium hydroxide is precipitated by sodium hydroxide in the absence of carbon dioxide. 100 c.c. of the water are made slightly acid with hydrochloric acid and concentrated to about 30 c.c. This residue is cooled and washed into a 100 c.c. stoppered cylinder with cold carbon dioxide-free water and made exactly neutral to methyl orange, after which 10 c.c. of *N*/10 sodium hydroxide solution are added to precipitate the magnesium. The mixture is diluted to 100 c.c. with cold carbon dioxide-free

water, the stopper of the cylinder replaced, the contents mixed and allowed to stand for some hours. A portion of the clear liquid is then withdrawn and titrated with decinormal acid. Since this method depends on the solubility of calcium hydroxide, it is obvious it may break down when large quantities of "calcium hardness" are present, unless the water be diluted sufficiently.

$$CaCl_2 + 2\ NaOH = 2\ NaCl + Ca\ (OH)_2,$$

$$i.e.\quad 2\ NaOH \equiv Ca\ (OH)_2 \equiv 2\ HCl.$$

Method of Kay and Newlands (*J.S.C.I.*, 1916, 445).—Calcium carbonate and magnesium carbonate are practically insoluble in 90 per cent. alcohol, but potassium carbonate is readily soluble. To 100 c.c. of the water are added 10 c.c. of $N/25$ potassium carbonate solution and the mixture is evaporated to dryness on a water-bath. The residue is mixed with 10 c.c. of 90 per cent. alcohol, warmed and filtered. The precipitate is washed three times with 90 per cent. alcohol, after which the filtrate is back-titrated with $N/50$ hydrochloric acid in the presence of methyl orange. If the precipitate be dissolved in an excess of decinormal acid, the total hardness can be determined by back-titration.

Determination of Free Carbon Dioxide.

Sodium bicarbonate is neutral to phenolphthalein. Hence, if a centinormal solution of sodium carbonate be added to a known volume of water containing phenolphthalein, the production of a pink colour denotes the removal of all the free carbon dioxide. Each cubic centimetre of $N/100$ sodium carbonate solution used is equivalent to 0·00022 grm. of carbon dioxide. In order to overcome the liability to errors due to variations in the relative concentrations of sodium carbonate and phenolphthalein, Czensny (*J.S.C.I.*, 1919, 476A) proposed the following modification: An $N/20$ solution of sodium carbonate is used containing 2·5 grms. of phenolphthalein per litre. From the volume of this solution used in titrating 100 c.c. of the water, 0·52 c.c. is deducted, and the remainder multiplied by 1·1 gives the free carbon dioxide as milligrammes per 100 c.c. of water.

Calculation of Quantities of Lime and Sodium Carbonate Required for Softening.

Let H_t be the temporary hardness, H_p the permanent hardness and H_m the magnesium hardness per 100,000 parts of water. Then

$$(H_t + H_m) \times 0{\cdot}56 = \text{lime required (CaO)},$$

$$H_p \times 1{\cdot}06 = \text{sodium carbonate required } (Na_2CO_3).$$

If only temporary hardness is to be removed, the quantity of lime required is $0{\cdot}56\ (H_t + H_m - H_p)$ when H_m is greater than H_p, but when H_m is not greater than H_p, only temporary hardness need be considered. Parts per 100,000 are the same as pounds per 10,000 gallons. In addition to the lime required for removing hardness, 1·273 parts are necessary for each part of free carbon dioxide.

The Analysis of Softened Water.

Softened water must be tested periodically, since any variation in the composition of the water itself or in the chemicals used, will make an adjustment of the softening formula necessary. The following determinations are made:

(1) Total hardness.
(2) Alkalinity towards phenolphthalein.
(3) Total alkalinity towards methyl orange.

The total hardness may be determined by means of soap solution or, in important cases, by the method described on p. 135. When titrating alkalinity a considerable volume (say 200 c.c.) must be used, and two experiments should be made. The results of the tests are expressed either as grains per gallon or parts per 100,000, both alkalinity and hardness being calculated to calcium carbonate. Thus, if 200 c.c. of water require 3 c.c. of decinormal acid to discharge the pink colour of phenolphthalein and then a further 3 c.c. after the addition of methyl orange, the alkalinity per 100,000 parts would be

(1) Phenolphthalein alkalinity, 7·5.
(2) Total alkalinity, 15·0.

The alkalinity of a softened water may be due to caustic alkali, sodium carbonate or bicarbonate of sodium, calcium or magnesium. When titrating with acid in the presence of phenolphthalein, the colour is discharged by the first drop of acid when only bicarbonates are present, since carbon dioxide will be liberated, thus

$$Ca\,(HCO_3)_2 + 2\,HCl = CaCl_2 + 2\,CO_2 + 2\,H_2O.$$

In the case of caustic alkali or sodium carbonate the discharge of the pink colour marks the completion of the reactions

$$NaOH + HCl = NaCl + H_2O,$$
$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

The acid required after the addition of methyl orange is that necessary to neutralise the bicarbonates formed during the first titration. If the phenolphthalein figure be exactly half the total alkalinity, it is evident that only sodium carbonate can be present. It follows that bicarbonates of calcium and magnesium are absent, and hence the water may be regarded as correctly softened, since all softened water contains a slight excess of sodium carbonate. The only thing is that the excess of sodium carbonate may be too great. This can be ascertained from the total alkalinity. If twice the phenolphthalein figure be *greater* than the total alkalinity, some caustic alkali must be present, the amount of which is measured by the difference between the total alkalinity and twice the phenolphthalein alkalinity. Thus, for example, if 200 c.c. of the water required 6·0 c.c. of decinormal hydrochloric acid to discharge the pink colour of phenolphthalein and a further 2·4 c.c. to change the colour of methyl orange, then 2·4 c.c. of decinormal acid are equivalent to half of the sodium carbonate present and (6 — 4·8) c.c., *i.e.* 1·2 c.c., are a measure of the caustic alkali. This would indicate that an excess of lime has been used, equivalent to 1·2 c.c. $N/10$ acid in 200 c.c., since in the presence of sodium carbonate, sodium hydroxide would be produced in accordance with the equation

$$Na_2CO_3 + Ca\,(OH)_2 = 2\,NaOH + CaCO_3.$$

Thirdly, if twice the phenolphthalein alkalinity be *less* than the total alkalinity, bicarbonates must be present and insufficient lime has been used. The deficiency is calculated in the following manner: If the phenolphthalein and methyl orange alkalinities were respectively 3·0 and 10·0 per 100 c.c., then 2 × 3·0 c.c. would represent the carbonate present and (10 — 6) c.c., *i.e.* 4 c.c. would measure the bicarbonates. The latter in terms of calcium carbonate, $CaCO_3$, would be 4 × 0·005 grm., *i.e.* 0·020 grm. per 100 c.c. or 20 parts per 100,000. The extra lime required to precipitate this would be 0·56 × 20, *i.e.*, 11·20 parts, per 100,000. When the quantity of lime used is correct, twice the phenolphthalein alkalinity would be practically equal to the total alkalinity. The *total hardness* is now determined. This will give some information about the correctness of the quantity of sodium carbonate used. If excess of sodium carbonate be present, the total alkalinity will be greater than the total hardness. On the other hand, if the hardness be greater than the total alkalinity, unremoved "permanent hardness" must be present, that is, insufficient sodium carbonate has been used, the deficiency being measured by the difference between the hardness and total alkalinity when both are expressed in terms of calcium carbonate. The following example will illustrate the method: Hardness 9·0, total alkalinity 6·0. The hardness exceeded the total alkalinity by 3·0 parts per 100,000. To remove this 3 × 1·06 parts of sodium carbonate will be required.

In the case of water which has been softened by means of zeolites or base-exchanging compounds, no determination is required except the total hardness. It is useful, however, to check the alkalinity by titration with decinormal acid in the presence of methyl orange.

Determination of Sodium Carbonate.

Some natural waters contain sodium carbonate. The first indication of its presence is given in the determination of the permanent hardness. When sodium carbonate is present the volume of decinormal acid used in the final titration will exceed the equivalent of the alkali originally added. This excess can be calculated to sodium carbonate, but it is better to make a separate test by evaporating about 250 c.c. of the water to dryness, extracting the residue with carbon dioxide-free water, filtering and titrating the filtrate with decinormal acid.

Determination of Iron.

Iron is determined by a colorimetric method. Half a litre of the water is acidified with hydrochloric acid and concentrated to about 30 c.c. The solution is washed into a Nessler cylinder, diluted to the mark and 1 c.c. of a freshly prepared dilute solution of potassium ferrocyanide added. The blue colour which is developed is then matched with that given by a standard solution of a ferric salt.

The Analysis of the Mineral Constituents of Water.

When a detailed analysis of the mineral salts present in water is required, the following procedure may be adopted:

From 250 to 500 c.c. of the filtered sample are acidified with hydrochloric acid, concentrated over a small flame and finally evaporated to dryness on a water-bath. The residue is baked for a short time to render silica insoluble. It is then extracted with warm hydrochloric acid and any *silica* which remains is filtered off, ignited and weighed. The filtrate and washings are made alkaline

with ammonia and boiled. The precipitate of the hydroxides of aluminium and iron is filtered off and washed. It is then dissolved in dilute hydrochloric acid, the solution made alkaline with ammonia and a little sodium peroxide (A.R.) added, after which the mixture is boiled again to expel hydrogen peroxide. The *iron* remains undissolved and is filtered off. The ferric hydroxide may either be ignited and weighed or dissolved in dilute hydrochloric acid and determined colorimetrically. The *aluminium* will be found in the filtrate as sodium aluminate. If the filtrate be acidified with hydrochloric acid and again made alkaline with ammonia, aluminium hydroxide will be precipitated and may be filtered off, ignited and weighed.

The filtrate from the united hydroxides of iron and aluminium is heated until it boils. About 2 grms. of powdered ammonium oxalate are then added and the mixture boiled for a minute to coagulate the precipitated calcium oxalate. This may be filtered off and ignited to calcium oxide, but it is much quicker and equally accurate to determine the *calcium* by titration with decinormal potassium permanganate solution. The calcium oxalate is filtered off on a Gooch crucible and washed well with hot water. The mat and precipitate are transferred to a flask or beaker and decomposed with excess of 10 per cent. sulphuric acid. The contents of the flask are now heated to about 60°C. and decinormal potassium permanganate solution run in until a permanent pink colour is obtained. Each cubic centimetre of decinormal potassium permanganate solution corresponds to 0·0028 grm. of calcium oxide or 0·005 grm. of calcium carbonate. *Magnesium* is precipitated in the filtrate from the calcium oxalate by the method of Schmitz (Treadwell, *Analytical Chemistry*, Vol. II., p. 67). The solution is made acid, heated until it boils, and treated with an excess of sodium phosphate. One-third of the solution's volume of 10 per cent. ammonia is added at once, the mixture allowed to cool, and after several hours filtered through a Gooch crucible. The precipitate is washed with 2·5 per cent. ammonia solution, dried, and ignited to magnesium pyrophosphate, $Mg_2P_2O_7$. The ignition should be gentle at first or it is difficult to obtain a white residue. ($Mg_2P_2O_7 \times 0{\cdot}3621 = MgO$).

The *alkali metals* are determined in a separate portion of the sample. A litre of the water is made slightly acid with hydrochloric acid and concentrated to about 100 c.c. This residue is treated with small quantities of barium hydroxide at the boiling point until a permanent alkaline reaction results. The precipitate is filtered off and washed. The filtrate and washings are heated to the boiling point and some ammonia, ammonium carbonate and ammonium oxalate are added. The mixture is again filtered and the precipitate washed. The filtrate will now contain only salts of the alkali metals and ammonia. The latter is removed by evaporating to dryness and igniting the residue gently. The residue after ignition is extracted with dilute hydrochloric acid and filtered. The filtrate is evaporated to dryness, the residue dried and weighed. It consists of *chlorides of potassium and sodium*. If the chlorine content be determined by titration with decinormal silver nitrate solution, the composition of the mixed chlorides can be calculated from the following relationship :

$$\begin{array}{c}\text{Difference between}\\ \text{molecular weights}\\ \text{of KCl and NaCl}\end{array} : \begin{array}{c}\text{Difference between weight of mixed}\\ \text{chlorides and weight of KCl corres-}\\ \text{ponding to chlorine found}\end{array} :: \begin{array}{c}\text{Molecular}\\ \text{weight of}\\ \text{NaCl}\end{array} : x,$$

where x = NaCl present in the mixed chlorides.

If preferred, the potassium may be determined gravimetrically and the sodium by difference. Potassium is determined as potassium perchlorate. To

the solution of the mixed chlorides in a small dish are added either a few drops of perchloric acid or about 10 c.c. of a 20 per cent. solution of this acid. The solution is evaporated on a hot plate until fumes of perchloric acid are given off. The mixture is then allowed to cool and the sides of the dish rinsed down with a little distilled water, after which a little more perchloric acid is added and the evaporation repeated. The contents of the dish are now allowed to cool and then washed on to a weighed Gooch crucible with industrial spirit. The precipitate is washed with a saturated alcoholic solution of potassium perchlorate, dried and weighed. ($KClO_4 \times 0{\cdot}340 = K_2O$).

Sulphates are determined in the usual manner by precipitation with barium chloride and weighing the barium sulphate produced. The weight of barium sulphate multiplied by 0·3430 gives sulphuric anhydride, SO_3.

Carbon Dioxide in Combination can be deduced from the temporary hardness, each cubic centimetre of decinormal acid used in the determination corresponding to 0·0022 grm. of carbon dioxide.

When the bases and acids have been determined, their probable combinations can be calculated. The sodium and potassium would be combined with chlorine. If any chlorine was left over it would combine with the magnesium. If any magnesium is left over it will probably be present as carbonate. The sulphuric acid will combine with calcium first and then with magnesium, whilst if there is too much calcium for the sulphuric acid the excess will be present as carbonate. The principle is that the strongest acids combine first with the strong bases and then with the weaker ones.

EFFLUENTS.

The principal determinations to be made in the analysis of trade effluents are :

(1) Free and "albuminoid" ammonia.
(2) Dissolved solids and suspended matter.
(3) Dissolved oxygen.
(4) Oxygen absorbed from the air and from potassium permanganate.
(5) Nitrates.

The determination of ammonia is made in the manner already described except that it may be necessary to dilute the effluent with ammonia-free water, since the Nessler test is only applicable to the determination of very small quantities of ammonia. Nitrates may be determined by the phenoldisulphonic acid method. Suspended matter is determined by filtering a measured volume of the effluent through a weighed Gooch crucible, and drying and weighing the residue ; the dissolved solids are determined in the filtrate.

Determination of Dissolved Oxygen.—Winkler's method is generally employed. Manganous hydroxide is produced by the interaction of manganous chloride and sodium hydroxide. The dissolved oxygen oxidises the manganous hydroxide and the manganic hydroxide formed liberates iodine from potassium iodide in the presence of hydrochloric acid :

$$\begin{aligned}
2\,MnCl_2 + 4\,NaOH &= 4\,NaCl + 2\,Mn\,(OH)_2,\\
2\,Mn\,(OH)_2 + O + H_2O &= 2\,Mn\,(OH)_3,\\
2\,Mn\,(OH)_3 + 6\,HCl &= 2\,MnCl_3 + 6\,H_2O,\\
2\,MnCl_3 + 2\,KI &= 2\,MnCl_2 + 2\,KCl + I_2.
\end{aligned}$$

If nitrites are present, they must be removed before making the determination. A measured volume of the effluent is treated with 1 c.c. of sulphuric acid and 2 c.c. of decinormal potassium permanganate solution. After standing for a few minutes the excess of potassium permanganate is removed by means of oxalic acid.

Winkler's determination is made in the following manner: A stoppered bottle of about 250 c.c. capacity is filled nearly to the stopper with the water, and 1 c.c. of a saturated solution of manganese chloride is added, being introduced by means of a pipette reaching nearly to the bottom of the bottle. 1 c.c. of a 33 per cent. solution of sodium hydroxide containing 10 per cent. of potassium iodide is introduced in the same way, the stopper replaced and the contents of the bottle mixed. After addition of the reagents, the liquid should reach the bottom of the stopper and no air be present. The contents of the bottle are next acidified with hydrochloric acid and the liberated iodine titrated with centinormal sodium thiosulphate solution (1 c.c. ≡ 0·00008 grm. O). There are some errors inseparable from the process, due chiefly to the difficulty in manipulation. These may be avoided to a considerable extent by the following modification proposed by the present authors (*J.S.C.I.*, 1926, 110 T): The bottle used is fitted with a two-holed rubber bung through which pass a capillary tap bent at right angles and a tap funnel also of very fine bore which reaches nearly to the bottom of the bottle. The bottle is graduated at 250 c.c. About 25 c.c. of petroleum, previously shaken with potassium permanganate and washed, are introduced into the bottle through the tap funnel, followed by 250 c.c. of the water. Air should now be expelled and the bent tap-tube filled with the petroleum. The reagents are then added through the tap funnel and mixed with the water by closing the taps and inverting the bottle. After acidifying, the contents of the bottle are poured into a flask and titrated. Completely aerated water contains about 1 part of dissolved oxygen per 100,000. A bad effluent may contain none.

Oxygen Absorbed from the Air.—A large bottle is half filled with the effluent and shaken for half a minute to aerate the liquid and distribute the suspended matter. Some tap water is aerated also, in the same way, and 300 c.c. of the aerated effluent are mixed with 1200 c.c. of the tap water. Four bottles of 350 c.c. capacity are filled with the mixture, allowed to stand for five minutes and then stoppered. The dissolved oxygen in two of these is determined at once. The other two bottles are incubated for 5 days at 65° F. and the dissolved oxygen again determined, nitrites first being removed in all cases. The oxygen absorbed is obtained by difference. Good effluents should not absorb more than 2·0 parts of oxygen per 100,000.

Oxygen Absorbed from Potassium Permanganate.—This determination is made in the same way as for water, except that a smaller volume of the sample is used.

CHAPTER XI.

ANALYSIS OF FIBRES.

COTTON.

THE analysis of raw cotton is seldom required. Cotton is never adulterated in the ordinary sense of the word, although it may contain an excess of moisture, leaf fragments and dirt. The *water* is determined by the conditioning process described in Chapter II. *Dirt* is generally estimated by opening out a weighed quantity of the cotton and shaking out the adventitious matter. *Mineral matter*, such as sand, may be identified by an examination of the ash. The normal *ash content* of different types of cotton of known origin and purity are given by Barnes (*J.S.C.I.*, 1916, 1191) in the following table:

Variety.	*Percentage of Ash.*
Sea Island,	1·18
Texas,	1·27
Arkansas,	1·33–1·67
Brown Egyptian,	1·50
Memphis,	1·92
Indian,	1·34–3·99

The incineration of cotton must be carried out at a low temperature, since salts of both sodium and potassium are present. The ash varies in colour from white or grey to reddish-brown. It is alkaline to phenolphthalein and consists of aluminium, calcium, magnesium, sodium, potassium, sometimes iron, combined with chlorine, sulphuric acid, phosphoric acid, silicic acid and carbonic acid.

The determination of the *phosphoric acid* (P_2O_5) according to Geake (*J.T.I.*, 1924, T 81) serves in certain cases to distinguish between cottons of different origin, the average percentages being approximately:

American,	0·05 per cent.
Sea Island,	0·07 ,,
Sakellaridis,	0·12 ,,
Egyptian (other than Sakellaridis),	0·09 ,,
South American,	0·07 ,,

After determining the moisture and dirt or sand, attention is directed particularly towards the following points: (1) Staple, (2) Evenness, (3) Fineness, (4) Neps, motes and bracts, (5) Strength of staple, (6) Unripe or dead cotton.

The Determination of Staple.—The term *staple* denotes the length of the individual hairs, raw cotton being classified as fine, medium or short, according to the average length of its hairs, the limits being given in the following table:

Fine,	Length of hairs $1\frac{1}{8}$ inches and over.
Medium,	,, ,, $\frac{7}{8}$ inch to $1\frac{1}{8}$ inches.
Short,	,, ,, below $\frac{7}{8}$ inch.

The measurement of the length presents no difficulty.

Evenness.—This is estimated by counting the percentage of hairs which are below the average length for the type of cotton under examination.

Fineness.—This is determined directly by measuring the *diameter* of the hairs by one of the methods described in Chapter II. Since, however, the diameter of a cotton hair always varies inversely with the length, the fineness can be judged by the proportion of short hairs present. The following table gives the relationship between length of hairs and diameter for common types of cotton :

Variety of Cotton.	Length of Hairs, in inches.	Diameter, in inches.
Sea Island, .	2 and over.	1/1500
Egyptian, . .	1·5 to 2	1/1500
South American,	1 to 1·5	1/1300
American, . .	0·9 to 1·25	1/1300
Indian, . .	0·6 to 0·8	1/1200

Neps, Motes and Bracts.—A *nep* consists of a tangled knot or mass of thin-walled hairs which on surface view exhibit a glazed appearance. They are objectionable in spinning, in yarns they tend to catch in knitting needles and cause breaks, whilst when the cotton is dyed the neps resist the action of the dyestuff and produce light-coloured patches. They have been studied exhaustively by Clegg and Harland (*J.T.I.*, 1923, T 125) from whose paper the illustration (fig. 40) of a nep has been taken. *Motes* are related closely to neps, consisting in woven goods of (*a*) a nep which is loosely incorporated in the yarn and which becomes detached, after printing, exposing a white patch beneath ; (*b*) a loose end of yarn which has become detached or removed to one side after printing, exposing a white patch beneath ; and (*c*) small white specks involving a large number of hairs all of which are dyed normally at other portions of their length. Motes consist commonly of fragments of the seed coat, with the short hairs attached to it, which have not been removed during the ginning process. *Bracts* are fragments of the leaf from the axil of which the cotton flower grows. *Unripe cotton* hairs are characterised by having thin cell walls, comparatively little twist and a badly defined lumen. *Dead hairs* appear to have no cell walls and to have collapsed completely, thus rendering the lumen invisible. Fig. 41 shows a number of cotton hairs of varying degrees of ripeness. The identification of unripe and dead cotton is assisted by the use of certain stains and reagents. Haller (*J.S.C.I.*, 1908, 976) found that when treated with Schweitzer's solution unripe hairs swell up but do not dissolve. They develop a blue colour with zinc chloriodide solution more quickly than ripe hairs. A solution of iodine in potassium iodide colours ripe hairs a dark yellowish-brown, whilst if unripe the hairs become light yellow. When immersed in a cold solution of sodium hydroxide unripe hairs do not loose their twist but only become more transparent. Herzog (*J.S.C.I.*, 1915, 487) showed that dead hairs are doubly refractive, showing colours under the polarising microscope, the insertion of a mica plate of 1·8 λ affording a ready means of detecting them ; ripe hairs remain bright in all positions, dead hairs show black and white portions according to their relative positions in the field, and unripe hairs show similar but less marked effects.

The Analysis of Unbleached Yarns and Fabrics.

Unbleached (or grey) cotton goods may contain in addition to cotton, such bodies as oil, size, lubricating mixtures and dirt. The size may contain starch, glue or gelatin, zinc chloride, magnesium chloride and soaps. A general analysis might be limited to the percentage of true cotton present or might be designed to determine the nature and quantity of the foreign ingredients. It is frequently of importance to a bleacher or dyer to know what loss of weight in the finished goods is due to the original impurities, especially in dealing with claims for short weight.

When the simpler form of analysis is sufficient, the following method may be adopted: The *moisture* is determined first by weighing a sample (about 10 grms.) in a weighing bottle and drying it at a temperature of about 105° C. until no

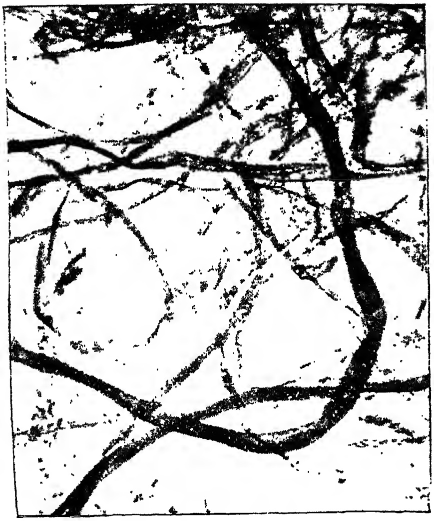


Fig. 40—A Nep.

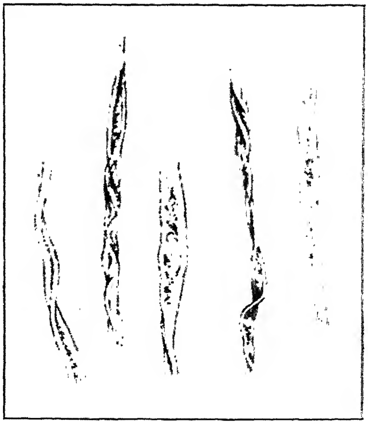


Fig. 41.—Ripe and Unripe Hairs.

more loss can be observed. A second portion of about 20 grms. is dried and extracted in a Soxhlet apparatus, or continuous extractor, benzene being the best solvent to use. The fat-free residue is washed several times with water to remove soluble salts. It is then placed in a flask of about 2 litres capacity, one litre of a two per cent. solution of sodium hydroxide is added and the contents of the flask boiled gently for about 2 hours, a vertical condenser being attached to the flask. The alkaline liquor is then drained off and the residual cotton washed several times in the flask with hot water until only traces of alkali remain. This operation removes starch, glue, proteins, and pectins. The cotton is now placed in chlorine water containing about one gramme per litre of chlorine or in a solution of sodium hypochlorite of about 1° Tw. strength. When no more bleaching effect can be observed, the cotton is removed, washed well with water, soaked for an hour in a 0·5 per cent. solution of hydrochloric acid, then washed until free from acid, dried at 105°

C. and weighed in a stoppered weighing bottle. The original and final weights are then calculated to weights at "correct condition" and the difference between the two gives the *loss on scouring and bleaching.*

When more detailed information is required than that obtained by the foregoing method, the following scheme of analysis may be adopted: The *moisture* and *ash* are determined and a second sample is dried and extracted in a Soxhlet extractor as before, but the solvent is now evaporated off, the residual *oil* dried, weighed, and examined further if necessary. The determination of *unsaponifiable oil* is described in Chapter XII. The *fat-free residue* is dried and weighed. It is then treated successively with water, boiling sodium hydroxide and bleaching liquors, as just described. The loss due to each process is determined separately by drying the cotton, after treatment and washing, until its weight is constant.

The Analysis of Bleached Cotton.

The standards for bleached cotton vary with the "degree of bleaching" required. The term "full bleach" is applied to the purest and most durable whites, the production of which demands almost complete freedom from impurities. The "half bleach" is used for goods when assistants or weighting materials are to be employed in the finishing processes and also for goods to be dyed: in such cases the requirements as to freedom from impurities are less severe. In the following sections it is assumed that the cotton under examination has been treated by the "full bleach" process. The following determinations are made:—

Ash.—This is determined in the usual manner and should not exceed 0·1 per cent. It should be white or grey in colour, a reddish tint indicating iron. When the ash is high the *calcium* content should be determined by dissolving in hydrochloric acid, filtering off silica, removing iron and aluminium with ammonia and then precipitating the calcium as oxalate and titrating the precipitate with decinormal potassium permanganate solution.

Oil and Wax.—Only traces should be found. Residual cotton waxes are the commonest cause of discolorations. *Soaps* of calcium and magnesium, which also cause discoloration, are determined in the manner described for wool.

Nitrogen.—This is determined by the Kjeldahl method described in Chapter V.

Matter Soluble in Sodium Hydroxide.—A well bleached cotton loses very little weight when boiled with sodium hydroxide solution. But if the lye boil has been incomplete, the loss may be considerable, amounting in some cases to 5 per cent. About 2 grms. of the sample are dried at 105° C., weighed, and boiled in a flask with 500 c.c. of 2 per cent. sodium hydroxide solution under a reflux condenser. The cotton is filtered off on a Gooch crucible, washed with boiling water until nearly free from alkali, then with dilute acetic acid, and finally with hot water until free from acid. It is then dried and weighed.

Acid and Alkali.—Acidity or alkalinity may be detected by means of selected indicators, the most sensitive being methyl red. If a cotton fabric is spotted with a 0·02 per cent. solution of this indicator and no change of colour is observed, it cannot contain more than 0·005 per cent. of either acid or alkali. A solution of potassium iodide, potassium iodate and starch was suggested by Briggs, which, in the presence of traces of mineral acid, becomes blue owing to liberation of iodine. A little starch is dissolved by boiling it with a solution of the two salts. When the solution is cold decinormal hydrochloric acid is added to it until a faint blue colour is produced. The mixture is now boiled until it becomes colourless and then allowed to cool. If cotton spotted with this reagent does

not develop a blue colour in five minutes it may be regarded as being free from acid. Coward and Wigley (*J. Soc. Dyers and Col.*, 259, 1922) investigated the sensitiveness of a number of indicators to acid and alkali. The results of their tests are given in the following table :

Indicator.	Percentage of Acid or Alkali Indicated.	Colour.
Thymol blue.	0·16 H_2SO_4.	Purple.
Methyl orange.	0·10–0·16 H_2SO_4.	Yellow-red.
Lacmoid.	0·06 H_2SO_4 and upwards.	Red.
	0·03–0·06 H_2SO_4.	Blue centre, red ring.
	0·02 H_2SO_4 and less.	Blue.
KI, KIO_3 and starch.	0·01 H_2SO_4.	Blue.
	0·005 H_2SO_4.	Red.
Methyl red.	0·005 NaOH.	Yellow.
Bromothymol blue.	0·05 Na_2CO_3.	Green.
	0·04 NaOH.	Blue.
Phenolphthalein.	0·12 NaOH.	Pink.

The quantitative determination of acid and alkali is not very easy, but the latter may be determined by titration of the fabric with centinormal hydrochloric acid in the presence of either phenolphthalein or bromothymol blue.

Coward and Wigley showed that acid could be titrated in a similar manner with $N/50$ sodium hydroxide solution. In either case a weighed portion of the sample is placed in a small flask together with some distilled water and the reagent is run in until the first colour change appears. The contents of the flask are then heated until boiling commences and the addition of the acid or alkali continued carefully, the liquid being boiled after each addition. Acid cannot be extracted readily from cotton by washing with water, repeated extractions being required, although it was shown by Coward and Wigley (*loc. cit.*) that it is extracted more readily when salt is present in the water. Sulphuric acid may be extracted by means of 95 per cent. alcohol, in which sulphates are insoluble. The cotton is placed in a Soxhlet or continuous extractor and extracted for about four hours. The alcohol is then evaporated off and the residue tested with barium chloride.

An indirect method similar to that of Procter and Hirst for the determination of mineral acid in leather is suitable also for cellulose fabrics. It depends upon the fact that the sodium salts of organic acids give sodium carbonate when incinerated. Hence, if cotton containing a free organic acid be treated with an excess of decinormal alkali and incinerated, the whole of the sodium carbonate added will be recoverable from the ash. If a mineral acid were present it would permanently neutralise its equivalent of sodium carbonate and there would be a deficiency in the ash corresponding to the amount of acid originally present. Thus, the method distinguishes between weak organic acids and strong mineral acids. About 3 grms. of the sample are placed in a platinum dish and wetted with distilled water, after which 25 c.c. of decinormal sodium carbonate solution are added. The contents of the dish are evaporated to dryness on a water-bath and then burnt at a low temperature until a char is obtained which will give a colourless extract with water. The charred mass is extracted with hot distilled water, being broken up carefully with a glass rod. It is then transferred to the filter paper and washed with hot water, the filtrate and washings being collected together in a flask. The filter paper and its contents are now put back into the platinum dish and burnt to an ash, which is washed into the flask containing

the extract. The liquid is cooled and titrated with decinormal acid, methyl orange being used as indicator. If no mineral acid were present in the cotton, exactly 25 c.c. of acid should be required, any sodium carbonate which has disappeared being the equivalent of a mineral acid such as sulphuric or hydrochloric acid.

The presence of a mineral acid may be established quite definitely in the following manner: An aqueous extract of the cotton is made and a portion of this titrated with centinormal alkali, phenolphthalein being used as indicator. A measured portion of the extract is then diluted with carbon dioxide-free water until it has a concentration of 0·01 *N*, or 0·001 *N*, and the *p*H value of this diluted solution is determined. The *p*H values of mineral acids such as hydrochloric acid or sulphuric acid would be approximately 2·0 and 3·0 respectively, those of weak organic acids much higher, in the case of acetic acid 3·36 and 3·89. If an acid of centinormal concentration has a *p*H value higher than 2·34, it cannot contain a strong acid. For really accurate work the *p*H value would have to be determined by an electrometric method, but in many cases reliable results may be obtained by the use of selected indicators.

Innes (*J.S.L.T.C.*, 1928, 266) suggested a method for the determination of free mineral acid based upon the effect of dilution upon the *p*H values of strong and weak acids respectively. The method is applicable to the examination of any aqueous extract containing small quantities of an acid. A strong mineral acid of *N*/100 concentration has a *p*H value of 2·0. If diluted to 10 times its volume with carbon dioxide-free water, the *p*H value is raised to 3·0. If diluted again ten times, the value is raised to 4·0, *i.e.*, dilution to ten volumes raises the *p*H value by one whole number. Weak organic acids behave differently, the *p*H value being raised by an amount not exceeding 0·6 by dilution to ten volumes. An aqueous extract of the sample is prepared. If the difference between the *p*H value of this solution and of the solution diluted ten times with water is about 0·5 or less, no strong mineral acid can be present. If the difference is 0·7 or more, then the presence of a strong acid is proved.

The following table shows the change in *p*H value of 0·1 *N*, 0·01 *N* and 0·001 *N* solutions of strong and weak acids:

Acid.	*p*H Value of Solution at 18° C.			Difference Figures.	
	0·1 *N*.	0·01 *N*.	0·001 *N*.	0·1 *N* and 0·01 *N*.	0·01 *N* and 0·001 *N*.
Hydrochloric.	1·03	2·01	3·00	0·98	0·99
Sulphuric.	1·21	2·08	3·01	0·87	0·93
Sulphurous,	1·48	2·34	3·09	0·86	0·75
Oxalic,	1·52	2·26	3·21	0·74	0·95
Formic,	2·35	2·87	3·45	0·52	0·58
Lactic,	2·43	2·95	3·52	0·52	0·57
Acetic,	2·87	3·36	3·89	0·49	0·53

Micro-chemical Determination of Combined Mineral Acids in Cotton.—Method of Ernich (*Microchemisches Practicum, München*, 1924), modified by Clibbens and Geake (*J. Text. Inst.*, 1927, T 168):

(*a*) *Sulphuric Acid.*—About 2 grms. of the cotton in pastille form, previously washed with distilled water and air dried at 110° C., are weighed accurately, moistened with 2 c.c. of 0·05 *N* sodium carbonate solution and dried again at

110° C. The dry cotton is burnt carefully, first at a low temperature and finally in a muffle at a temperature not above 550°–600° C. The ash is treated with 3 or 4 drops of water, followed by 0·7 c.c. of 2 N nitric acid. The excess of acid is removed by evaporation on a water-bath and the residue ignited carefully over a microburner. The residue is dissolved in 0·7 c.c. of 1·0 N hydrochloric acid, the solution filtered by suction through a micro-filter of fritted Jena glass, 1 cm. in diameter, and the filter washed. The filtrate and washings (about 5 c.c.) are collected in a hard glass beaker of 6 to 7 c.c. capacity, heated to about 100° C. in a vessel jacketed with the vapour of boiling toluene and 0·7 c.c. of a hot filtered solution of 0·1 N barium chloride solution added. After digesting for an hour the solution is separated from the precipitate by drawing it under suction through a micro-filter immersed in it, the bulk of the precipitate being left in the beaker, which is then washed four times by inverse filtration with about 2 c.c. of hot water. The filter plate is made of the finest grade fritted Jena glass, 8 mm. in diameter, and the glass walls of the filter are ground down flush with the plate (see fig. 42). After washing, the filter is detached from the

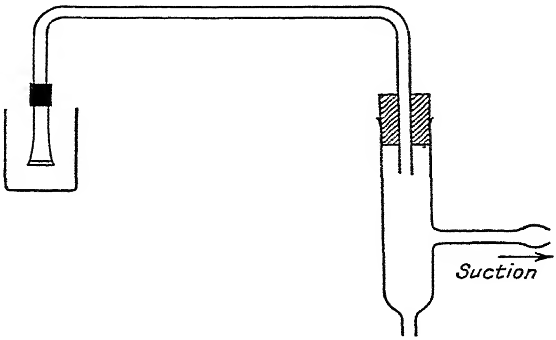


Fig. 42.—Micro-filter.

suction tube and is dried in a beaker in a vessel jacketed with boiling aniline. The filter and beaker are weighed on a balance sensitive to 0·01 mgm.

(*b*) *Hydrochloric Acid.*—The cotton (2 grms.) is moistened with 2 c.c. of 0·05 N sodium carbonate solution, dried at 110° C. and ashed as described above. Owing to the presence of sodium carbonate, a considerable residue of carbon may remain. The ash is treated with 0·7 c.c. of water, filtered off and washed, the filtrate acidified with dilute nitric acid, a slight excess of 0·1 N silver nitrate solution added, and the mixture digested for an hour as before and cooled. It is then filtered through the micro-filter, the precipitate washed four times with 2 c.c. of cold water, dried at the temperature of boiling aniline and weighed.

The Identification of Hydrocellulose and Oxycellulose.—Hydrocellulose is the first product of the hydrolysis of cotton by acids. Oxycellulose is an oxidation product containing both ketone and carboxylic groups. The distinction between these two bodies is not always easy, particularly when " tendering " has been produced by the drying-in of mineral acids. The following are some of the qualitative tests which have been proposed :

1. *Methylene Blue Test.*—Both hydrocellulose and oxycellulose adsorb

Methylene Blue and other basic dyestuffs from a cold aqueous solution. Well-bleached cotton is only stained by Methylene Blue and the colour is removed by boiling with water: hence if bleached cotton be stained deeply by a cold solution of Methylene Blue (or Safranine) and the colour remains after washing, either hydrocellulose, oxycellulose, or both, are present. This test has an important quantitative application which will be described later.

2. *Knecht's Test.*—Both oxycellulose and hydrocellulose have less affinity for direct dyestuffs, such as Diamine Sky Blue, than normal cotton. A sample of the fabric is dyed with Diamine Sky Blue. The presence of patches which have a decreased affinity for the dyestuff indicates the presence of either hydrocellulose, oxycellulose, or both. A fresh sample of the cotton is boiled with a 5 per cent. solution of sodium hydroxide, washed, and dyed as before. Oxycellulose (sodium salt) now absorbs the dyestuff but hydrocellulose either does not or has a decreased affinity for it.

3. *Knapp's Test* is based, also, on the lower affinity of oxycellulose for direct dyestuffs. The sample is dyed in a boiling aqueous solution of Benzopurpurin, which is very sensitive to mineral acids. The dyed sample is rinsed and placed in a beaker with some distilled water and treated carefully with dilute hydrochloric acid until the colour becomes blue. It is now rinsed in hard water to neutralise the acid. The red colour reappears on the cotton, but oxycellulose remains blue-black in colour.

4. *Ermen's Test.*—A suspension of Indanthrene Yellow is prepared by dissolving its paste in concentrated sulphuric acid, pouring the solution into cold water and neutralising the acid. A few drops of this suspension are added to some 10 per cent. sodium hydroxide solution and the material to be tested is saturated with this liquid and squeezed lightly. It is then held over a beaker containing boiling water. If either hydrocellulose or oxycellulose be present, a deep blue stain appears within one minute, well-bleached cotton showing no colour for at least five minutes. If, after steaming, the sample be washed, scoured, again washed, and then rubbed with soap, the unaffected dyestuff is removed, but where reduction has taken place the colour remains fixed firmly.

Another test due to Ermen (*J. Soc. Dyers and Col.*, 1928, 303) is as follows: Two solutions are required, (*a*) ferric sulphate 20 grms., ammonium sulphate 25 grms., in 100 c.c. of water, (*b*) potassium ferricyanide 33 grms., in 100 c.c. of water. When making a test, 5 c.c. of (*a*) and of (*b*) are added to 250 c.c. of water and the mixture heated to the boiling point. The flame is removed and the cotton immersed in the liquid for one minute. It is then rinsed in dilute sulphuric acid and finally in water. A deep blue colour due to Prussian blue indicates oxycellulose. All bleached cotton gives a faint colour.

5. *Phenylhydrazine Test.*—Since oxycellulose contains ketone groups, it reacts with phenylhydrazine. Paranitrophenylhydrazine, dissolved in acetic acid, is more sensitive and stains oxycellulose a yellow colour.

6. *Schwalbe's Test.*—Both hydrocellulose and oxycellulose reduce Fehling's solution. The sample is boiled with water to remove soluble bodies. It is then placed in a mixture of equal volumes of Fehling's solution and distilled water and the mixture boiled gently for 15 minutes. If hydrocellulose or oxycellulose be present, the cotton becomes red, owing to the formation of cuprous oxide. The quantitative application of this test will be described later.

7. *Schwalbe and Becker Test.*—This test distinguishes between hydrocellulose and oxycellulose. Some of the sample is ground with a little distilled water and a drop of methyl orange solution is added. In most cases the colour remains yellow, but if strongly acid oxycelluloses are present it becomes brown. A

few cubic centimetres of brine are added. In the case of cellulose or hydrocellulose the colour remains unchanged, but if oxycellulose be present a deep wine-red colour is produced.

8. *Harrison's Test.*—Silver nitrate is added to a solution of sodium thiosulphate, the mixture being stirred vigorously, and then sodium hydroxide solution added so as to obtain a liquid containing 1 per cent. of silver nitrate, 4 per cent. of sodium thiosulphate and 4 per cent. of sodium hydroxide. The material is boiled or padded with this solution and then steamed. The parts containing hydrocellulose or oxycellulose become stained. The effect is increased if the material be heated first with a one per cent. solution of phenylhydrazine in glacial acetic acid and washed thoroughly with dilute acetic acid.

9. *The Nessler Test.*—The sample is sprinkled with Nessler solution. A well-bleached sample gives only a barely perceptible change in colour. The rapid production of a yellow colour indicates damage, whilst if the colour passes quickly through orange to grey, the cotton should be rejected.

The Quantitative Determination of Oxycellulose or "Degree of Bleaching."—The most important test in the case of bleached cotton is the determination of the degree of bleaching, which is measured largely by the amount of oxycellulose present in the sample. Oxycellulose reduces Fehling's solution owing to the presence of carbonyl groups in it. Cellulose itself has no reducing action on Fehling's solution. Hence the reducing power of the cotton may be taken as a measure of the degree of bleaching. But oxycellulose contains carboxyl groups, also, which are formed by the oxidation of either carbonyl or aldehyde groups. These carboxyl groups give the cotton an affinity for basic dyestuffs such as Methylene Blue. Hence, if a sample of bleached cotton has a marked affinity for Methylene Blue, probably it has been overbleached. There are, however, two distinct types of oxycellulose. Knecht and Thompson (*J. Soc. Dyers and Col.*, 1922, 132) showed that in the initial stages of the oxidation of cellulose, aldehyde or ketone (*i.e.*, reducing) groups are produced rapidly, but that as the oxidation proceeds these tend to become oxidised into carboxyl groups. The first type of oxycellulose has a high reducing power but a comparatively small affinity for Methylene Blue, whilst the second kind has a large affinity for Methylene Blue accompanied by a lower reducing power.

Birtwell, Clibbens and Ridge (*J. Text. Inst.*, 1925, T 13) found that the type of oxycellulose produced in bleaching depends upon the reaction of the bleaching liquor used. On the alkaline side of neutrality the formation of acid groups predominates, whilst on the acid side ketone groups are chiefly produced. Hence both reducing power and affinity for Methylene Blue must be determined, in order to obtain reliable information about the degree of bleaching. These determinations are known as

(1) The "copper number" determination.

(2) The "Methylene Blue number" determination.

A third test known as the "viscosity test" is also of importance. It was proposed by Ost (*Z. angew. Chem.*, 1911, **24,** 1892) and investigated fully by Farrow and Neale (*J. Text. Inst.*, 1924, T 157) and Clibbens and Geake (*ibid.*, 1928, T 77). It depends upon the fact that very small differences in the chemical or physical condition of cotton are capable of being detected by the change which they produce in the viscosity of a solution of the material in cuprammonium solution (Schweitzer's reagent). The viscosity of the solution

is a guide to the nature of the treatment which the material has undergone. Although definite values for viscosity cannot be established, the determination of the viscosity of the cuprammonium solution before and after any process of treatment gives very valuable information, and the method is very suitable for the control of scouring and bleaching operations.

The Copper Number.—This is defined as the number of grammes of copper which are reduced by 100 grms. of the sample when boiled with Fehling's solution under prescribed conditions. Its determination depends upon the fact that oxycellulose contains ketone groups and acts therefore like dextrose as regards copper solutions. Pure cellulose has a very small copper number, varying from 0·2 to 0·3. Knecht's oxycellulose (*J. Soc. Dyers and Col.*, 1920, 251) gives 14·2. The copper number of overbleached cotton may therefore vary from 0·3 to 14·2.

The determination of the copper number was proposed first by Schwalbe. His method (*J.S.C.I.*, 1907, 548) was as follows: Two portions of the sample, each weighing about 3 grms., are taken and the moisture determined in one of them. The other is cut into small pieces, which are placed in a flask together with 100 c.c. of Fehling's solution and 200 c.c. of water, and the contents of the flask boiled under a reflux condenser for 15 minutes, agitating frequently. The hot liquid is filtered off, with the aid of a pump, the residue being washed with boiling water. The cuprous oxide on the filter and cotton is then dissolved in nitric acid and the copper determined by a suitable method. The disadvantage of this method is that cotton adsorbs copper salts from their solutions. This is allowed for by soaking a similar weight of the cotton in cold Fehling's solution and water and after washing with water determining the copper which the sample retains. This is not very satisfactory, however, since it is not certain that the same amount of copper will be adsorbed at ordinary atmospheric temperatures as at the boiling point. Knecht and Thompson (*J. Soc. Dyers and Col.*, 1920, 255) overcame the difficulty by the following modification of Schwalbe's method: After boiling the sample with Fehling's solution, the mixture is filtered through a Gooch crucible and the residue washed with boiling water as before. The crucible and its contents are then placed in a beaker containing from 1 to 2 grms. of iron alum dissolved in dilute sulphuric acid, the liquid being stirred until the cuprous oxide has dissolved. The crucible is then removed and washed and the liquid filtered, the residue being washed with water. The combined filtrate and washings contain ferrous sulphate in exactly equivalent amount to the cuprous oxide originally present.

$$Fe_2(SO_4)_3 + H_2O = 2\,FeSO_4 + H_2SO_4 + O,$$
$$Cu_2O + O + 2\,H_2SO_4 = 2\,CuSO_4 + 2\,H_2O.$$

The ferrous sulphate is determined by titration with decinormal potassium permanganate solution. From the equations it is seen that 1 atom of iron is equivalent to 1 atom of copper, and hence 1 c.c. of $N/10$ potassium permanganate solution is equivalent to 0·0063 grm. copper. This method is much simpler than that of Schwalbe and adsorbed copper salts do not affect the titration, but when oxycellulose is boiled with sodium hydroxide solution it is decomposed to a certain extent with the formation of compounds which have no reducing action on Fehling's solution. In order to prevent this, the sample should not be allowed to come into contact with boiling caustic alkali. Several methods have been proposed with this object in view. The best of these is due to Braidy (*Rev. Gén. Mat. Col.*, 1921, **25**, 35). It has been investigated by Clibbens and Geake (*J.T.I.*, 1924, T 27), who recommended it as avoiding both the error

due to adsorbed copper and that due to auto-reduction on boiling oxycellulose with ordinary Fehling's solution. The following solutions are required :

(*a*) 100 grms. of pure crystalline copper sulphate dissolved in 1 litre of water.

(*b*) 50 grms. of sodium bicarbonate and 350 grms. of crystalline sodium carbonate dissolved in 1 litre of water.

(*c*) A solution containing 100 grms. of iron alum and 140 c.c. of concentrated sulphuric acid per litre.

(*d*) Standard $N/25$ potassium permanganate solution.

Immediately before beginning the analysis, 5 c.c. of solution (*a*) are run from a burette into 95 c.c. of solution (*b*), the mixture heated to the boiling point and poured over 2·5 grms. of the material to be tested, which is contained in a conical flask of a capacity slightly more than 100 c.c. The cotton is distributed throughout the liquid by means of a glass rod and any air bubbles present are allowed to escape. The flask is then immersed in a constant level water-bath which is kept boiling rapidly. The flask should be immersed deeply in the water and care must be taken to cover the top of the bath sufficiently to prevent cooling of the reaction mixture by currents of cold air. The flask is allowed to remain in the boiling water for exactly three hours, its contents then filtered with suction and the cotton washed first with dilute sodium carbonate solution and then with hot water. The cuprous oxide is then dissolved by treating the cotton on the filter with 15 c.c. of solution (*c*) and then with a further 10 c.c. and again with 10 c.c. if necessary. The cotton is washed with $2N$ sulphuric acid and the combined filtrates are titrated with $N/25$ potassium permanganate solution. The only drawback to this method is the long time required for reduction of the Fehling's solution.

Heyes (*J.S.C.I.*, 1928, 90 T) described a microchemical method which enables reliable results to be obtained with so little as 0·25 grm. of the sample.

The "Silver Number" is determined sometimes, but has no advantage over the "copper number." In this test the cotton is boiled with a solution of silver nitrate and sodium acetate and the quantity of reduced silver is determined by titration with potassium thiocyanate (Rinse, *J. Ind. Eng. Chem.*, 1928, 1228).

Kauffman's Method.—A new method proposed by Kauffman (*J. Soc. Dyers and Col.*, 1924, 128) consists of boiling the sample with an aqueous solution of sodium hydroxide and then determining the quantity of potassium permanganate required to oxidise the dissolved organic matter.

The Methylene Blue Test.—An approximate estimation of the quantity of oxycellulose present is given by the depth of colour produced when a fabric is treated by the Methylene Blue qualitative test. The quantitative application of the method has been studied exhaustively by Constance Birtwell, Clibbens and Ridge (*J.T.I.*, 1923, T 297), who described the following process: From 1 to 2 grms. of the cotton, cut into small pieces, are shaken for 18 hours at room temperature in a glass-stoppered bottle with 50 c.c. of a solution of Methylene Blue hydrochloride containing approximately 0·4 millimole per litre. Some of the solution is then withdrawn and the remaining Methylene Blue determined colorimetrically, using a standard solution of Methylene Blue (0·2 millimole per litre) for comparison.

The Methylene Blue may be determined also by titration with Naphthol Yellow S or titanous chloride. The first method depends upon the fact that when a solution of Naphthol Yellow S is run into one containing Methylene

Blue, a reddish-brown precipitate is formed, the blue colour of the solution becoming less intense and finally yellow, but the end-point of the reaction is rather difficult to observe.

Ristenpart (*J.T.I.*, 1924, A 254) uses Ostwalt's scale of notation, in which the standard for a normal white is a matt surface of barium sulphate, 100 stages of grey being distinguished between this and black. On this scale, a commercial bleached cotton has a value of 70 to 80 degrees of white. The variation in the degree or percentage of white in a sample dyed with Methylene Blue is taken as a measure of the degree of damage. A comparison may be obtained in the form of a ratio between the degree of whiteness of the original sample and of the sample dyed with Methylene Blue. If this ratio be Q for the bleached goods and Q_u for the unbleached goods, then the Methylene Blue value is expressed as the difference produced by bleaching :

$$M = \frac{Q - Q_u}{Q_u},$$

M being termed the "Methylene Blue number." This, however, is defined usually as the number of millimoles of Methylene Blue absorbed by 100 parts of cotton.

The dyeing is carried out by immersing pieces of the material (5 sq. cms.) in 50 c.c. of a cold 0·001 per cent. solution of Methylene Blue for ten minutes, rinsing and drying in contact with a smooth surface. In comparing the whiteness of the dyed material with standard whites, Ristenpart recommends the use of Ostwalt light filter No. 2 for the production of equal colour tone.

Birtwell, Clibbens and Ridge (*loc. cit.*) arrived at the following conclusions with regard to this test : (*a*) The ash content, or more strictly the alkalinity, affects the absorption of the dye. (*b*) Different cottons do not behave in the same way. Thus, Egyptian cottons always show a higher absorption than American cottons. (*c*) When the quality of the cotton remains the same, the absorption is determined by the efficiency of the bleaching operations. In particular, if the scouring process removes the non-cellulose impurities insufficiently, a high absorption results, which is not corrected by the subsequent "chemic." (*d*) The addition of soap or olein to the kier results in an increased absorption of Methylene Blue by the bleached material when these bodies are left in the cotton, as for example, in the form of insoluble soaps. (*e*) Processes such as "calendering" and "mercerising," which alter the surface properties or degree of dispersion of cotton cellulose, have no effect on the absorption.

Knecht and Thompson (*J. Soc. Dyers and Col.*, 1921, 270) showed that increased affinity for Methylene Blue may be caused by combined sulphur in the cellulose molecule. Kauffman (*Textilber*, 1925, **6**, 591) demonstrated that the depth of colour obtained with the dye does not depend primarily upon the oxycellulose content, since goods containing oxycellulose dye equally deeply when the oxycellulose has been removed by boiling with alkali or water. The absorption of Methylene Blue is determined partly by the pH figure, an increasing hydrion concentration causing a diminished absorption, whilst increasing hydroxyl-ion concentration raises the absorption (*cf.* Pelet Jolivet, *Die Theorie des Farbenprozesses*, and Birtwell, Clibbens and Ridge, *loc. cit.*).

From the foregoing facts, it appears that the Methylene Blue test is valuable chiefly as a differential test, its value depending upon determining the absorption before and after processing. Its application to material of unknown origin and treatment is liable to give misleading information. Moreover, certain

types of oxycellulose with high reducing powers have comparatively little affinity for Methylene Blue.

Birtwell, Clibbens and Geake express the Methylene Blue absorption in terms of millimoles per 100 grammes of cotton, and from 0·5 to 0·6 may be regarded as a normal figure.

The Viscosity Test.—The employment of the viscosity of a solution of the cotton as a test is due to Ost (*Zeitsch. angew. Chem.*, 1911, **24**, 1892). The method was investigated critically by Farrow and Neale (*J. Text. Inst.*, 1924, T 157) and Clibbens and Geake (*J. Text. Inst.*, 1928, T 77), from whose papers details are taken: The cuprammonium solution used contains 15 grms. of copper, 240 grms. of ammonia and less than 0·5 grm. of nitrous acid per litre. It is prepared in the following manner: A large earthenware bottle, fig. 43, of about 5 litres capacity, is surrounded by ice and closed with a cork through which passes an iron centrifugal stirrer and an iron inlet tube. The

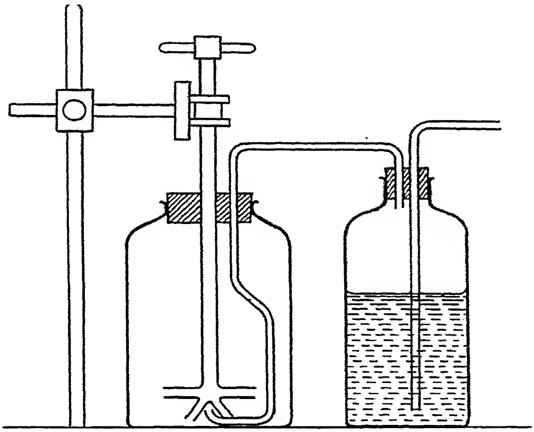


Fig. 43.—Apparatus for Preparing Cuprammonium Solution.

latter ends in an upturned jet which conducts air into the trumpet-shaped mouth of the stirrer. A mixture containing 2·6 litres of concentrated ammonia (density 0·880), 0·4 litre of water and 3 grms. of cane sugar is stirred at about 400 revolutions a minute with 180 grms. of precipitated copper which has passed through a 60-mesh sieve and air is blown in at the rate of 10 litres an hour through a wash bottle containing ammonia solution of density 0·900. The approximate copper content of the solution can be checked by colorimetric comparison with a sample of standard concentration, both being diluted to ten volumes with water. The preparation requires about 5 hours, or one hour when oxygen is used instead of air; the proportion of nitrous acid is high in the latter case. After standing for half an hour the solution is syphoned off and allowed to settle in a stoppered bottle, the residual copper being washed and used again. The clear liquid is again syphoned off and tested. The copper is determined by titration with potassium iodide and sodium thiosulphate, ammonia by titration with sulphuric acid in the presence of methyl red, and nitrous acid by means of a nitrometer. The cuprammonium solution is stored in a blackened bottle provided with a

tubule and tap at the bottom and connected at the top through a vessel containing alkaline permanganate solution to a gas holder or Kipp containing nitrogen.

The viscometer is shown in fig. 44, and it is employed also for dissolving the cotton. The instrument has an internal diameter of 1 cm. and a length of approximately 26 cm., whilst the lower capillary D is 2·5 cm. long, 0·088 cm. in internal diameter and 0·6 cm. in external diameter. The wide portion is etched with two rings B and C at heights 6·2 and 24·2 cm. vertically above the flat end of the lower capillary tube and the upper end of the instrument is closed with a rubber stopper carrying a second capillary E, the dimensions of which are unimportant. A steel cylinder F, 2·7 cm. long, made from $\frac{1}{8}$-inch steel rod, is provided, the lower half of which is notch-shaped, as shown in the figure, its weight being $5·6 \pm 0·2$ grms. The test is made with a solution containing 0·5 grm. of dry cotton in 100 c.c., and for each instrument a record is kept of the weight of material required to yield a solution of this concentration when dissolved in the volume of cuprammonium solution necessary to fill the viscometer. The cotton is divided finely. Yarn is cut across into lengths not exceeding one-sixteenth of an inch, and cloth in narrow widths is cut in a diagonal direction to break down both warp and weft threads. After the lower capillary has been closed with a short length of pressure tubing and a clip, the weight is placed in position and the viscometer about three-quarters filled with cuprammonium solution. A few drops are run out at the bottom, and the predetermined weight of cotton added and mixed rapidly with the solvent by means of a thin glass rod. The viscometer is then filled completely with cuprammonium solution and the stopper inserted, so that the excess of liquid overflows through the upper capillary and rubber tube, thus displacing air. The clip is now closed, the stopper wired into position, and the viscometer, wrapped in black cloth, is bound to the spokes of a bicycle wheel rotating at such a rate that during each half revolution the steel cylinder falls from end to end of the liquid column. About four revolutions per minute are generally sufficient. For the instrument described, 20 c.c. of solution are sufficient, so that approximately 0·1 grm. of cotton is used. When solution is complete, the viscometer is removed from the wheel, the lower clip and rubber tube withdrawn and the instrument hung in a wider tube in a thermostat at 20° C. When it has acquired this temperature it is placed in the jacket G, which is supported vertically in the thermostat. The upper clip is now opened, the stopper removed, and the solution allowed to flow freely through the lower capillary. The time in seconds required for the meniscus to fall from C to B is noted. The viscometer is standardised with a mixture of glycerin and water of specific

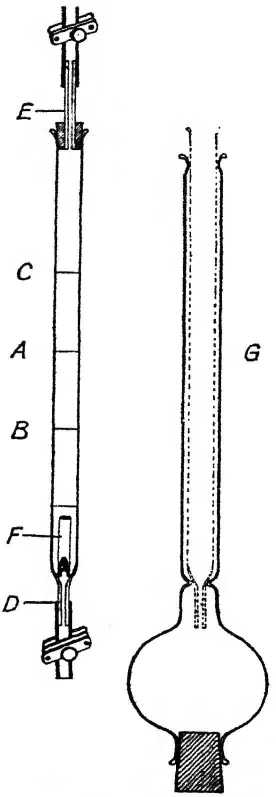


Fig. 44.—Viscometer.

gravity 1·1681 in air at 20° C. compared with water at the same temperature. For routine work the viscosity of the cotton solution is expressed as the ratio of its time of flow to that of the glycerin solution, but for other purposes, the rate of flow is expressed in the form of absolute fluidity, *i.e.* the reciprocal of the viscosity in poises. For this the constant of the instrument is divided by the time of flow of the cotton solution.

At 20° C. the specific gravity (d) of the standard glycerin solution is 1·1681 and the fluidity (F) in absolute units is 6·83. If the time of flow in the standard viscometer be t seconds, then the constant of the instrument $C' = 1{\cdot}075\ dFt$. When cotton is highly tendered, and the solution very fluid, a correction is applied for the kinetic energy of the liquid. This may be done by subtracting from the time actually observed an amount obtained from a table given and which increases as the time of flow decreases.

The Detection of Chlorine and Chloramines.—Chlorine, hypochlorites and chloramines all liberate iodine from potassium iodide in the presence of dilute sulphuric acid, but chlorine and hypochlorites are decomposed by hydrogen peroxide, whilst chloramines are not. If cotton be treated with a dilute acidified solution of hydrogen peroxide, washed, and then potassium permanganate solution be added very carefully to decompose the excess of peroxide, only chloramines can remain undecomposed; hence if cotton still liberates iodine from potassium iodide, their presence is proved.

Special Tests.—*Liability to Yellow.*—This may be tested for by steaming the sample for half an hour in an autoclave at about 1 atmosphere pressure. Freiberger moistens the cotton with a solution of sodium ricinoleate and steams at the ordinary pressure.

Wood Gum Value.—Piest (*J.S.C.I.*, 1913, p. 17) describes this as the percentage of matter soluble in a cold 5 per cent. solution of sodium hydroxide after prolonged standing. It is a complex function including small quantities of fatty acids, gum, and the soluble products of overbleaching (*i.e.*, alkali-soluble oxycellulose). Normally bleached cotton gives a value of from 0·5 to 1 per cent.

The Hydrate Copper Value is the percentage of cupric oxide absorbed from cold Fehling's solution (Piest). This is regarded as indicating the state of hydration of the cellulose, being specially pronounced in the case of "mercerised" cotton, normal (0·5) in the case of oxycellulose, and particularly low for hydrocellulose.

The Acid Value.—This is the amount of sodium hydroxide neutralised on boiling for half an hour with a 1 per cent. solution. It also is a complex function, indicating primarily the chemical modification due to oxycellulose and hydrocellulose in approximately equal degree, and secondarily the specific susceptibility of the cellulose itself to alkaline hydrolysis. It is particularly low in the case of cellulose which has been treated already with strong alkali (*e.g.*, "mercerised" cotton) and which is not otherwise modified by drastic oxidising or acid treatment which would increase the tendency to hydrolysis.

The Determination of α-Cellulose.—The term α-cellulose is applied to that portion of wood pulp or cotton linters which is insoluble in a 17·5 to 18 per cent. solution of sodium hydroxide. The determination is of great importance in the examination of the raw materials used for the manufacture of artificial fibres. The cellulose which is soluble in 17·5 per cent. sodium hydroxide is divided further into β-cellulose and γ-cellulose, the former being precipitated when the alkaline solution is acidified. Wood pulp or cotton linters contains as a rule 88 to 90 per cent. of α-cellulose, 10 per cent. of β-cellulose and 0·2 per cent. of γ-cellulose. That portion of the sample which is dissolved by the caustic alkali is often termed "hemicellulose." The method of determination

commonly used is that proposed by Jengten: 1 grm. of the sample is triturated with 25 c.c. of 17·5 per cent. sodium hydroxide solution for 30 minutes, then sucked dry on a Gooch crucible by means of a pump, the residue broken up, washed with 4 per cent. sodium hydroxide solution and then with water. This residual α-cellulose is either dried and weighed or determined by titration by means of a solution of potassium dichromate. The residue is placed in a 250 c.c. beaker, dissolved in 72 per cent. sulphuric acid, the solution washed into a 100 c.c. flask and made up to 100 c.c. with acid of the same strength. A measured volume of this solution (10 c.c.) is treated with 10 c.c. of potassium bichromate solution (90 grms. per litre) and 60 c.c. of 72 per cent. sulphuric acid. The mixture is boiled gently for five minutes, cooled on ice and the excess of bichromate titrated with standard ferrous ammonium sulphate solution, a blank experiment being carried out simultaneously. The reaction is represented by:

$$C_6H_{10}O_5 + 6\,O_2 = 6\,CO_2 + 5\,H_2O.$$

Hence one part of oxygen is equivalent to 0·844 part of cellulose.

The cellulose may be determined also, according to Birtwell and Ridge (*J. Text. Inst.*, 1928, 341 T), by measuring the carbon dioxide produced in the oxidation.

Kiesel and Semiganovsky (*Ber.*, 1927, **60,** (B) 333), recommend the determination of cellulose by saccharification: The dry cellulose is treated with from 7 to 10 times its weight of 80 per cent. sulphuric acid at atmospheric temperature for two and a half hours. Water is then added in the proportion of 15 c.c. to each cubic centimetre of acid used and the resulting solution is heated for 5 hours on a steam bath. Cellulose is converted quantitatively into dextrose under these conditions. Ketoses and pentoses should be absent.

Bubeck (*Papier Fabr.*, 1926, **24,** 66-71, from *J.S.C.I.*, 1926, B 579) showed that when cellulose is mercerised with 17·5 per cent. sodium hydroxide, filtered and washed, the sum of the hemicellulose in the filtrate, as determined by the chromic acid method, and of the undissolved α-cellulose, is less than 100. This is due to the more dilute alkali formed during washing dissolving cellulose which is not dissolved by the mercerising alkali. A higher value for hemicellulose is obtained if the mercerising alkali be diluted before filtering, and the maximum value when the diluted solution contains 9 grms. of sodium hydroxide per 100 c.c. The amount extracted depends also to a small extent on the duration of the mercerisation, increasing by about 0·2 per cent. between 0·5 and 1·5 hours. It is more dependent on temperature and diminishes by about 2 per cent. between 12° C. and 27° C. The following method of determination is recommended: 3 grms. of the sample are mercerised at 18° C. with 20 c.c. of 17·5 weight-per cent. sodium hydroxide solution. After half an hour, 80 c.c. of 8 to 9 volume-per cent. sodium hydroxide are added and the mixture filtered. The residue is washed with 50 c.c. of 8 to 9 volume-per cent. sodium hydroxide, and then with water, acetic acid, and again water. It is then dried and weighed. *Hemicellulose* may be determined in an aliquot part of the filtrate by oxidation with chromic acid. Bubeck proposed to re-define hemicellulose in accordance with this method of determination.

Waentig's method (*J.S.C.I.*, 1922, 935 A).—3·5 grms. of the sample are dried at 105° C., weighed and steeped in a porcelain mortar with 50 c.c. of 17·5 per cent. sodium hydroxide solution for 45 minutes, the mass being worked to a uniform paste with the pestle. 50 c.c. of water are then stirred in and the paste transferred to a Büchner funnel, 8 to 10 cm. in diameter, covered with a fine cotton cloth filter. The paste is washed on to the filter with 200 c.c.

of 8 per cent. sodium hydroxide solution and sucked as dry as possible. The residue is then treated with 50 c.c. of 5 per cent. acetic acid, sucked dry again, transferred to the mortar, broken up and stirred with another 50 c.c. of 5 per cent. acetic acid. The cellulose is collected on the filter, washed with water until neutral to litmus, and dried, at first on a clock glass, then at 105° C. in a stoppered weighing bottle. The *hemicellulose* may be determined in the filtrate by making up to a definite volume and boiling with sulphuric acid and potassium bichromate.

It is difficult to obtain concordant results unless the conditions of working are always the same. Berggrist (*Papier Fabr.*, 1929, **27,** 119) emphasises the following points: (1) The temperature of the determination should be maintained at 20° C. by the use of a thermostat, and the wash water should also be at 20° C. (2) After addition of diluting water, filtration and washing must be carried out as quickly as possible, a suitable filtering medium being a piece of coarse linen placed in a Büchner funnel. (3) For dilution of the sodium hydroxide solution after mercerising, the same quantity of water (300 c.c.) should always be used. (4) Five minutes should suffice for the kneading operation if care be taken.

In a report (*J. Soc. Dyers and Col.*, 1929, 122) issued by a sub-committee of the Division of Cellulose Chemistry of the *American Chemical Society*, it is recommended that, where good grades of cotton or pulp are used, there should not be any occasion for a dispute about the α-cellulose content if the following tentative standard method of estimation is adopted:

Preparation or Conditioning of Sample.—Cotton is not subjected to a preliminary treatment. Pulps are cut into pieces, 1·25 cm. square. The material to be used in estimations of *moisture* and *α-cellulose* content is placed in a glass stoppered bottle for 48 hours.

Method.—About 3 grms. of the sample are placed in a 250 c.c. Pyrex beaker; 35 c.c. of 17·5 per cent. sodium hydroxide solution (free from carbonate) are added, and the whole allowed to stand for 5 mins. The pulp is macerated for 10 mins. with a glass rod flattened at one end into a disc 1 cm. in diameter, whilst 40 c.c. of the sodium hydroxide solution are added intermittently in portions of 10 c.c. at 20° C. The beaker is covered with a watch glass and placed in a water-bath at 20° C. for 30 mins. 75 c.c. of distilled water are next added and the contents of the beaker passed through a Gooch crucible having fine perforations. The cellulose is allowed to form its own mat, and filtration is repeated if necessary. The residue is washed with 750 c.c. of distilled water at 20° C., using suction. 40 c.c. of 10 per cent. acetic acid are added, and the material allowed to stand for 5 mins. The acid is removed by suction, the α-cellulose washed with distilled water until free from acid, placed in a tared, flat, glass-stoppered weighing bottle, opened out and dried for 6 hours at 105° C. The first constant consecutive weight obtained after one-hour heating intervals following the initial drying is taken as the correct figure. The α-cellulose content is calculated on the oven-dry weight of the material. Duplicate 3 grm.-samples are used for the determination of moisture.

WOOL.

The methods used in the analysis of wool depend upon the object of the examination. Sometimes attention is directed to one particular point only, sometimes a general analysis is required. When the latter is desired the following determinations are made:

Moisture.—About 5 grms. of the sample are weighed in a stoppered weighing bottle and dried at a temperature of from 100° to 105° C. for about 3 hours. The sample is then again placed in the weighing bottle and reweighed. It is then put back in the oven for a further hour and again weighed, this procedure being repeated until the weight is constant.

A more accurate method is described by Barritt and King (*J. Text. Inst.*, 1926, T 392). A weighing bottle (fig. 45) is used in which the stopper is replaced by a tap which opens or closes an inlet and outlet tube as desired. When the tap is open a current of air can be drawn through the wool, entering at the bottom of the bottle, and on turning the tap through an angle of 90°, the bottle is completely closed. The bottle containing the weighed wool is placed in an electrically-heated oven at 104°–106° C. and a current of dry air (dried by passing through sulphuric acid and over calcium chloride) is drawn through the bottle. After 2 hours the tap is closed, the bottle transferred to a desiccator for half an hour and then weighed. It is then heated again for half an hour and reweighed, this procedure being repeated until the weight is constant.

Ash.—About 5 grms. of the sample are incinerated in a silica dish in the usual manner.

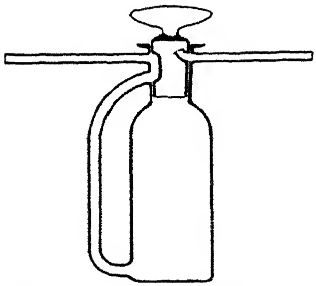


Fig. 45.—Special Weighing Bottle.

The Determination of Oil and Soap.—Oil is determined in the usual manner by drying a weighed portion of the sample and extracting it with petroleum ether in a Soxhlet or continuous extractor. The unsaponifiable oil in the residue is separated by the method described for fats. The fat-free residue is used for the determination of soaps. These may be present either as soluble sodium or potassium soaps or as insoluble calcium and magnesium compounds. The residue is extracted with hot absolute alcohol in a continuous extractor for about 3 hours. The alcohol solution is filtered, if necessary, and evaporated to dryness. The residue is treated with hot distilled water to dissolve the soap and the solution washed into a separating funnel. A definite volume of decinormal hydrochloric acid is added and the liberated fatty acids extracted with ether. The ether is washed with a little water to remove mineral acid, the washings being added to the rest of the acid liquor. The ether solution is then evaporated, and the residue dried and weighed, this giving the weight of fatty acids present in the wool. The acid liquor is titrated with decinormal sodium hydroxide solution, methyl orange being used as indicator. Each cubic centimetre of acid which is used is equivalent to 0·0031 grm. of sodium oxide, Na_2O. The weight of the fatty acids multiplied by 0·97 gives the corresponding fatty acid anhydrides, and the sum of these and the sodium oxide is the soap.

Calcium and magnesium soaps, if present, will remain in the fabric. They are decomposed by soaking the sample for an hour in dilute hydrochloric acid, after which the excess of acid is removed by washing with distilled water. The sample is then dried and again extracted with ether in a Soxhlet extractor. The residue, after evaporating off the solvent, will consist of fatty acids derived from calcium and magnesium soaps.

Although alcohol is a satisfactory solvent for soap, it is not possible to recover from wool the same amount of soap as is placed in it, since there is distinct evidence that some of the alkali of the soap combines with or becomes

adsorbed by the wool substance itself, leaving free fatty acid on the fibre. Atmospheric carbon dioxide is able to decompose soap into an "acid soap" and an alkali carbonate, and this affects the analysis.

Matter Soluble in Water.—The residue after extraction of oil and soap is extracted repeatedly with small quantities of hot water, the washings being collected in a litre flask. The liquid is finally cooled, diluted to one litre, well mixed and filtered. An aliquot portion of the filtrate is evaporated to dryness in a weighed dish on the water-bath, the residue dried and weighed. If the dry residue is incinerated, both soluble organic and inorganic matter may be determined. The remainder of the filtrate is used for any qualitative tests which may be necessary.

Sulphur.—When wool is damaged by acids, sulphuretted hydrogen is given off, whilst alkali damage causes the production of soluble sulphides. Chlorination changes some of the sulphur into sulphuric acid. The sulphur content of undamaged wool is comparatively constant and may be taken as 3·3 per cent. Any marked lowering of this percentage would indicate that hydrolysis of the protein substance had taken place.

The following method (Trotman and Bell, *J.S.C.I.*, 1926, 10 T) is suitable for the determination of the sulphur and is a slight modification of the Benedict-Denis process: The reagent used is made by dissolving 25 grms. of crystalline copper nitrate, 25 grms. of sodium chloride and 10 grms. of ammonium nitrate in 100 c.c. of water. About 0·2 grm. of the wool is warmed with a little pure sodium hydroxide solution until just dissolved. A few drops of bromine are added and after a few minutes the solution is neutralised with nitric acid. 10 c.c. of the reagent are then added and the mixture evaporated to dryness. The residue is heated to dull redness for 10 minutes, cooled, dissolved in dilute hydrochloric acid and filtered. The sulphate in the filtrate is determined by precipitating with barium chloride.

Rimington (*J.S.C.I.*, 1930, 139 T) criticised the foregoing method and recommended the following modification: Samples of 1 grm. and 0·25 grm. are taken for moisture and sulphur determinations respectively. The sulphur is determined as follows: 10 c.c. of hydrochloric acid (2 parts concentrated acid and 1 part water) are placed in a silica crucible, which is heated on a hot plate until its contents begin to simmer. The wool is then introduced and the crucible warmed until solution is complete. The Benedict-Denis reagent (10 c.c.) is then added and the liquid evaporated to dryness on a water-bath. A further 4 c.c. of the reagent are added and evaporated, after which the test is completed as described above. It may be mentioned that when wool is dissolved in hydrochloric acid some sulphuretted hydrogen is evolved. The method of Trotman and Bell was designed to prevent this loss.

Barritt and King (*J. Text. Inst.*, 1926, T 386) are of opinion that the Carius method is more accurate than that just described. They recommend the following process: About 3 c.c. of fuming nitric acid (sp. gr. 1·53) are transferred by means of a long funnel and pipette to the bottom of a Carius tube, and the wool transferred by means of forceps and pushed down the tube to within about 6 inches of the bottom by means of a glass rod. The tube is sealed in the usual manner, and estimations carried out in duplicate for each sample. The tubes are heated together in the Carius furnace, and during a period of about 1½ hours are raised to 200° C. and maintained at this temperature for eight hours. Each tube is allowed to cool overnight and opened by softening the tip with a Bunsen flame, a slight pressure being found in the tube. After withdrawing from the furnace and cutting off the ends, the tubes are gently warmed to drive off dissolved gases, and the contents washed out into beakers, evaporated

to dryness (on steam) with the addition of hydrochloric acid, this procedure being repeated to remove all traces of nitric acid, which is detrimental to the sulphate estimation. About 100 c.c. of hot distilled water are added and the liquid filtered to remove any traces of glass introduced when opening the tube. The filtrate is now acidified with dilute hydrochloric acid, heated to boiling and precipitated by the slow addition of 50 c.c. of boiling $N/20$ barium chloride solution. After keeping hot for some hours and allowing to stand overnight, the barium sulphate is collected on a weighed Gooch crucible in the usual way.

Sulphurous Acid.—Wool which has been stoved contains as a rule residual sulphurous acid, the determination of which may be of importance in some cases. The method used is to distil off the sulphurous acid by means of steam or a stream of carbon dioxide, pass it into either bromine water or hydrogen peroxide and determine the sulphuric acid formed by weighing as barium sulphate. The weight of barium sulphate obtained multiplied by 0·274 gives sulphur dioxide. Hydrogen peroxide is to be preferred as the oxidising agent. Some organic substances, such as wool, are liable under the treatment described to give off volatile sulphur compounds which are oxidised to sulphuric acid by bromine but not by a cold solution of hydrogen peroxide.

About 10 grms. of the sample to be tested are cut into small pieces, weighed, and placed in a distilling flask of about one litre capacity. A little water is added and a few drops of phosphoric acid to decompose any sulphites which may be present. The flask is then connected with a steam can and the delivery tube to a vertical condenser, the lower end of which dips beneath the surface of a little 10-volume hydrogen peroxide in a flask or beaker. The hydrogen peroxide must, naturally, be free from sulphates. The air in the distilling flask should first be displaced by carbon dioxide. A rapid current of steam is then passed through the apparatus for 20 minutes, after which some barium chloride solution and hydrochloric acid are added to the distillate to precipitate the sulphuric acid. After standing for 12 hours the precipitate is filtered off, washed, ignited and weighed.

Rothenfusser (*Analyst*, 1929, 770) collects the distillate in a mixture of 5 c.c. of a filtered 5 per cent. solution of benzidine in 96 per cent. alcohol, 5 c.c. of 30 per cent. acetic acid and 5 c.c. of 10-volume hydrogen peroxide. The insoluble benzidine sulphate is filtered off cold, washed three times with 5 c.c. of water, dried at 105° C. for thirty minutes and weighed. The factor for conversion into sulphur dioxide is 0·234.

Chlorine.—Wool which has been treated by a process for making it unshrinkable, may contain sometimes residual chlorine, either in the form of chloride or chloramine. When organic matter is burnt to an ash some of the chlorine is lost unless special precautions are taken. A weighed quantity of the sample is placed in a silica dish and covered with a dilute solution of pure sodium carbonate or lime. The mixture is evaporated to dryness on a water-bath and the residue ignited gently until a completely charred mass is obtained which will give a colourless extract with water. The charred residue is treated with water, the mixture filtered and the insoluble matter washed. The filter paper and carbon are then returned to the dish and burnt to an ash at a low temperature. This ash is again extracted with water. The combined extracts and washings are acidified with nitric acid and the chlorine precipitated as chloride with silver nitrate, the precipitate being filtered off on a Gooch crucible and weighed. Or, the solution is neutralised carefully with acetic acid and then titrated with decinormal silver nitrate solution.

An alternative method of determination is to heat the wool with fuming

nitric acid in the presence of a slight excess of solid silver nitrate. When a colourless solution is obtained, it is diluted with water and the silver chloride filtered off on a Gooch crucible, dried and weighed.

Detection of Chloramines.—The wool is soaked for some time in a cold slightly acid solution of hydrogen peroxide in order to remove any chlorine or hypochlorite, if present, chloramines remaining unchanged. The sample is then washed with water and treated with a cold dilute solution of potassium permanganate acidified with sulphuric acid as long as decolorisation occurs. Any excess of permanganate is decomposed by adding a little oxalic acid, after which the sample is washed and soaked in a solution of potassium iodide and dilute sulphuric acid. If chloramines are present iodine will be liberated slowly, but more quickly on warming the solution. If the chlorine be determined in this manner, a measure of the chloramines will be obtained.

Determination of Acid.—The determination of acid in wool is difficult. A method sometimes adopted is to soak a weighed quantity of the sample in a known volume of decinormal ammonia in a stoppered bottle for some time and then determine the unneutralised ammonia by titration of an aliquot portion of the liquid with decinormal acid. But wool adsorbs a certain amount of the ammonia, thus rendering the result unreliable. It is not possible to extract the whole of the acid with either water or alcohol. According to Hirst and King (*J.T.I.*, 1926, T 101) the ammonia method can be made reasonably accurate by introducing a correction factor to allow for the ammonia adsorption, or by carrying out a blank test on neutral wool. Another difficulty is that acid soaps or fatty acids are included as mineral acid. A better method is to place 10 grms. of the sample in water at 60° C. and after 15 minutes add 1 grm. of finely powdered magnesium carbonate. The mixture is allowed to stand overnight and then filtered. The wool is then washed with distilled water and the filtrate and washings are made up to a definite volume. A portion of the solution is then treated with barium chloride and hydrochloric acid and the barium sulphate filtered off and weighed. If the wool contains soluble sulphates these will be included also.

Meunier and Rey (*Rev. Gén. Mat. Col.*, 1924, **28,** 66-67) state that the following method is accurate: 5 grms. of the wool are steeped for 24 hours in 200 c.c. of $N/20$ sodium bicarbonate solution. The supernatant liquid is decanted off and the wool washed four times with 50 c.c. of distilled water. The liquor and washings are boiled with 50 c.c. of $N/5$ sulphuric acid and cooled. The excess of acid is then determined by back-titration with $N/5$ sodium hydroxide solution in the presence of phenolphthalein.

Another similar method, which is used sometimes, is to wash the wool with several quantities of $N/20$ sodium carbonate solution, the total volume used being noted accurately. The wool is then washed several times with distilled water, the washings being added to the sodium carbonate solution. The liquid is made up to a definite volume and the unneutralised sodium carbonate determined by titration with $N/20$ sulphuric acid.

Hirst and King (*loc. cit.*) pointed out that whilst acids and alkalis are both adsorbed by wool, neutral salts are not. Hence by converting the acid into a neutral salt it should be possible to remove it completely. At the same time it is necessary that the reagent used should not be adsorbed by the wool. These conditions would be fulfilled by an insoluble acid which forms a soluble non-hydrolysible salt with the alkali metals, and terephthalic acid and sodium terephthalate were found by Hirst and King to fulfil these conditions and can be applied to the determination of both acid and alkali in wool. The type of

action involved by the employment of these reagents is indicated by the following equations :

$$C_6H_4\,(COONa)_2 + H_2SO_4 \rightarrow Na_2SO_4 + C_6H_4\,(COOH)_2,$$
$$C_6H_4\,(COOH)_2 + 2\,NaOH \rightarrow 2\,H_2O + C_6H_4\,(COONa)_2,$$
$$C_6H_4\,(COOH)_2 + Na_2CO_3 \rightarrow H_2O + CO_2 + C_6H_4\,(COONa)_2,$$
$$C_6H_4\,(COOH)_2 + 2\,C_{17}H_{33}COONa \rightleftharpoons 2\,C_{17}H_{33}COOH + C_6H_4\,(COONa)_2,$$

in which it is seen that acids are converted into their soluble sodium salts and insoluble terephthalic acid, while alkalis are converted into the soluble alkali terephthalates which are only adsorbed by wool to a very slight degree, and, therefore, easily removed by washing. In the case of soaps, however, one of the products of the reaction is a fatty acid, which will be adsorbed to some extent by the wool.

This method is very interesting from a theoretical point of view and a suitable subject for research work, but the cost of terephthalic acid is so great as to preclude the possibility of adopting the process for routine work. The following details are taken from the paper of Hirst and King.

Determination of Acid or Alkali Content by Means of Terephthalic Acid.—Terephthalic acid is acid to all indicators whose colour change takes place at pH $> 4{\cdot}5$ and alkaline to indicators the colour change of which takes place at a lower pH value, *e.g.* bromophenol blue and methyl orange. The employment of bromophenol blue, which has a range from $p\mathrm{H} = 2{\cdot}8$ to $4{\cdot}6$ over which it changes from yellow through bluish-grey to bluish-purple, is recommended by Hirst and King in preference to methyl orange (in view of its more striking colour change) in the titration of terephthalic acid.

The procedure adopted by Hirst and King is based upon the fact that on adding acid, previously standardised against alkali, and using bromophenol blue as indicator, to a liquid containing terephthalic acid and sodium terephthalate, the indicator remains purple until the whole of the sodium terephthalate is converted into terephthalic acid, when the colour change commences. The terephthalic acid solution is prepared by adding the acid, with shaking, to caustic soda solution, until a small permanent excess remains, and then filtering. The solution is just acid (yellowish-green) to bromothymol blue.

The determination is carried out either by heating a weighed quantity of the wool with an excess of sodium terephthalate solution to 60° C. for 15 minutes and allowing to stand for three hours, or by allowing the mixture to stand overnight at the ordinary temperature. In either case the solution is poured off, the sample washed and pressed several times and the united solutions filtered. A measured excess of $N/10$ sulphuric acid is then added, the solution again filtered and titrated with $N/10$ sodium hydroxide solution, with bromophenol blue as indicator. For routine tests it is simpler and sufficiently accurate to analyse an aliquot portion of the original liquor.

Determination of Alkali.—Determinations of alkali are affected by the presence of soaps. Hence an essential preliminary is the removal of these bodies. This is generally effected by extraction with alcohol. According to Hirst and King (*loc. cit.*) reasonably accurate results are obtained when the wool after extraction with alcohol is warmed in neutral distilled water and titrated with standard acid in the presence of phenol red or phenolphthalein. The titration must be carried out cautiously, with constant stirring and warming from time to time, until the indicator shows a permanent change.

It has been found by the present authors that *cyclo*hexanol is a good solvent for the removal of soap, and that it has no solvent action on either sodium

hydroxide or sodium carbonate. About 5 grms. of the dried sample are heated with the solvent on a water-bath for about an hour and the liquid poured off. Two more extractions are made in the same manner, after which the wool is placed in warm water and the alkali titrated as just described.

The *terephthalic acid method* of Hirst and King is more accurate. A weighed quantity of the wool is treated with water and a known quantity of terephthalic acid is added. The mixture is warmed to 60° C. and allowed to stand for four hours. A known excess of standard acid is then added and the liquid filtered and titrated back with sodium hydroxide.

It should be noted that sodium hydroxide, sodium carbonate and soap are all co-estimated by this method, as seen by the equations

$$2\,NaOH + C_6H_4\,(COOH)_2 = 2\,H_2O + C_6H_4\,(COONa)_2,$$
$$Na_2CO_3 + C_6H_4\,(COOH)_2 = H_2O + CO_2 + C_6H_4\,(COONa)_2.$$
$$2\,C_{17}H_{33}COONa + C_6H_4\,(COOH)_2 = 2\,C_{17}H_{33}COOH + C_6H_4\,(COONa)_2.$$

Calcium soaps are also decomposed by terephthalic acid, and when these are present, a separate determination of the calcium must be made and the corresponding quantity of calcium soap calculated and allowed for.

Determination of Acid and Alkali Content of Wool with Indicator Dyestuffs.—It has been found by King (*J. Soc. Dyers and Col.*, 1927, **43,** 321) that indicators of the sulphonphthalein type, introduced by Clark and Lubs, possess excellent dyeing properties and that when dyed on wool they retain their sensitiveness to acids and alkalis, but in diminished degree. A much greater range of acidity is shown by these indicators when dyed on wool than when used in solution in the ordinary way; for example, 0·25 per cent. solutions of sulphuric acid change thymol blue completely when used in solution, whereas to produce the same change on wool requires a solution of 15 times this strength. The indicator-dyestuffs used by King were chosen from the sulphonphthalein indicators with the addition of lacmoid, as shown in the following table. All the indicators can be satisfactorily used from an acetic acid bath (1 per cent. acetic acid on the weight of the wool), starting in the cold and raising very slowly to the boiling point.

Indicator.	Applications.	Colour Change (with increasing conc. of acid).	Per cent. H_2SO_4 Indicated (on dry wool).	Approx. Strength of Equilibrium Solution. Normality.	Percentage Strength.
Acid	*Range.*				
Thymol blue (A).	Carbonising.	Yellow–orange-red–Magenta red.	4·5–7	N/10–N/1·2	0·5–4·0
Bromophenol blue (B).	H_2SO_4 in dye bath.	Blue–greenish-blue–yellow.	3–5	N/500–N/10	0·01–0·5
Lacmoid (C).	Acid milling.	Slate blue–puce red.	1·5–3·5	N/1000–N/50	0·005–0·1
Bromocresol purple (D).	For leaving wool faintly acid.	Purplish–dirty blue–yellow.	0–2	Neutral–N/1000	Neutral–0·005
Bromothymol blue (E).	Neutralising.	Bluish-green–yellow.	0–1	Neutral–N/10000	Neutral–0·0005
Alkaline Range.					
Bromothymol blue.	Scouring, Washing-off and Soap milling.	Bluish-green–bright blue.	Register successively over a range from neutrality to 5 per cent. Na_2CO_3 solution.		
Phenol red.		Red–yellow.			
Cresol red.		Yellow–purplish-red.			
Thymol blue.	Piece scouring with alkali.	Yellow–slate blue.			

In employing these indicator-dyestuffs it is desirable to use the minimum amount commensurate with a good colour change on making acid or alkaline, and also to use chemically equivalent quantities rather than equal weights, in order to have the same reacting quantity of each indicator per unit weight of wool. A convenient basis is stated by King (*loc. cit.*) to be 0·02 per cent. of Phenol Red (which has the lowest molecular weight of the series) and to use quantities of the other members of the series proportionate to the molecular weights :

Indicator.	Molec. Wt.	Molec. Ratio.	N/10 NaOH per 1 grm. Colour.	0·02 per cent. Soln. per 100 grms. Wool.
Bromophenol Blue, .	670	1·89	16 c.c.	189 c.c.
Bromothymol Blue, .	624	1·76	17 ,,	176 ,,
Bromocresol Purple, .	540	1·52	20 ,,	152 ,,
Thymol Blue, . .	466	1·31	22 ,,	131 ,,
Cresol Red, . .	382	1·08	28 ,,	108 ,,
Phenol Red, . .	354	1·00	30 ,,	100 ,,

In the case of lacmoid a heavier shade is necessary and 0·8 per cent. on the weight of the cloth is a suitable quantity.

All the indicator-dyestuffs mentioned in the first table are fairly fast to sulphuric acid in cold solution up to a strength of 5 per cent. Those marked A to E in the first part of the table are fast to one hour's exposure to 0·5 per cent. sodium carbonate solution but lose their colour on prolonged exposure. With ordinary soap solutions they are, however, reasonably fast. With the exception of lacmoid (C) all the indicators can be rendered yellow on cloth by an appropriate amount of acid. In this form the dyed cloth is reasonably fast to light and can be stored without deterioration.

The Detection of Damage in Wool.—Since the proteins of wool are attacked readily by chemical reagents such as alkalis, acids and chlorine, and by moulds and other micro-organisms, it is possible to produce damage by almost every process used in the treatment of the fibre. It is a well-known fact that when wool has been damaged by any one process it becomes more susceptible to damage during succeeding processes, the effect being cumulative.

The recognition of damage is very simple when serious destruction of the fibre has occurred ; on the other hand it is not easy to detect incipient damage which, if not checked, may lead to marked deterioration of the finished goods. The following methods of examination are employed :

Microscopic Examination.—In undamaged wool fibres the epithelial scales will be intact, with sharply-defined outline and plainly visible free serrated edges, and owing to their opacity the cortex is invisible.

Typical undamaged fibres are illustrated in fig. 46.

When the fibres are attacked by acids, the first indication of damage is the formation of striations due to the wrinkling of the epithelial scales. This is followed by the swelling-up of the scales, the appearance of furrows, and finally the disintegration and disappearance of the epithelium and exposure of the cortex.

The action of alkalis is not so apparent, since the cortex is attacked first, and by prolonged treatment with dilute alkali it may be dissolved almost completely without altering materially the appearance of the epithelial scales. Hence slight damage, which nevertheless would be sufficient to render the fibre unstable and susceptible to attack by hydrolysing agents, may be undetected when microscopic examination is relied on alone.

Damage due to chlorine is accompanied by the gradual eating away of the epithelium, the outline of the scales becoming progressively fainter and the scale itself more transparent until ultimately it disappears, the cortex is exposed to view and sometimes even partially disintegrated. These stages are illustrated in fig. 47. Damage produced by other oxidising agents is very similar in appearance to that produced by chlorine and the same may be said of bacterial damage.

When wool is examined under the microscope the following precautions should be observed. A few fibres should be removed from the sample, spread out evenly on a slide and soaked in water until they are thoroughly wet. The cover glass is then pressed down carefully and the slide examined with a $\frac{1}{4}$- or

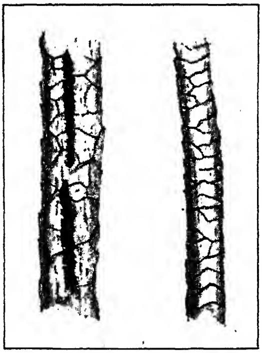


Fig. 46.—Wool Fibres.

Fig. 47.—Damaged Wool Fibres.

$\frac{1}{6}$-inch objective. Only a moderate illumination should be used and very careful focussing is necessary.

Microscopic examination may be assisted by dyeing the fibres lightly, particularly with a dyestuff which is sensitive to acids or alkalis, or by mounting the sample in a semi-saturated solution of chlorine water, as proposed by Allwörden :

Allwörden's Reaction.—An interesting observation first made by Allwörden (*Zeitsch. angew. Chem.*, 1916, **29,** 77) is that on subjecting undamaged wool to the action of chlorine water, a microscopical examination of the preparation will show the formation of a series of globular excrescences protruding through the epithelial scales along the length of the fibre. This was assumed by Allwörden to be caused by the swelling of a carbohydrate constituent of the wool fibre situated between the cortex and the epidermal layer as a result of

the action of chlorine. Allwörden further considered that this substance, which he termed "elasticum," is the chief factor affecting the behaviour of wool in fulling and finishing and its resistance to acids, but, on the other hand, is readily removed by alkalis. According to Allwörden's generalisations the behaviour of wool when treated with chlorine should therefore give an indication of the extent to which the fibres had been damaged by alkalis. Thus, the appearance under the microscope of relatively few swellings on mounting the fibres in half-saturated chlorine water would indicate incipient damage by alkalis, whilst the formation of no swellings at all would indicate serious damage.

In the hands of different workers this reaction has led to contradictory results. Whilst the appearance of the swellings may be taken as a definite indication that no damage by alkalis has occurred, wool known to be undamaged does not always give the globular swellings. The explanation of this fact may be found in the work of Speakman and Goodings (*J.T.I.*, 1926, **17,** T 607), who, by improved technique, showed that the swellings or blisters commence to grow at the free edges of the scales and then continue above the surface of the scales along the fibre; the product appears to be some protein substance formed by the action of the chlorine on the wool. Since the action of chlorine on wool is to produce the property of unshrinkability, and since the unshrinkability produced by the action of equal concentrations of chlorine on different wools differs considerably, the contradictory nature of the results obtained by Allwörden's test is intelligible.

Staining Tests.—The fact that damaged fibres react abnormally with dyestuffs may be utilised as a means of investigation.

If wool be soaked in 5 per cent. sulphuric acid, pressed, dried for one hour at 80° C., then washed with water until free from acid, only the damaged fibres will have an affinity for acid dyestuffs.

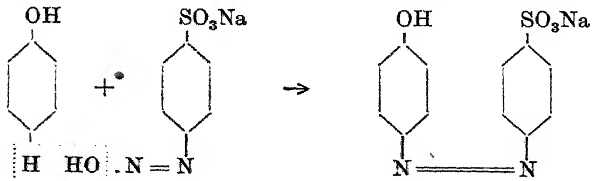
Blackshaw (*J. Soc. Dyers and Col.*, 1928, 298) recommended the use of Acid Scarlet 4 R Extra BDC, which stains alkali-damaged wool in a cold bath. Sieber (*Text. Merc.*, 1927, 406) found Cotton Red 10 B (Colour Index No. 495) to be capable of indicating damaged fibres. The sample is immersed in a boiling 0·1 per cent. aqueous solution of the dyestuff and then examined microscopically. Fibres damaged by acid or alkali and those showing mechanical damage are coloured from pink to dark red according to the extent of the damage.

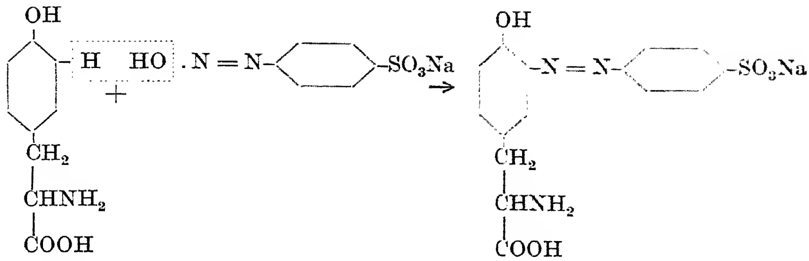
Pauly (*J. Physiol.*, 1904, **4,** 508) used an alkaline solution of diazotised sulphanilic acid, which stains the cortex a reddish-brown colour, but only when the epithelium has been damaged. A quantitative application of the Pauly reaction has been described by Rimington (*J.T.I.*, 1930, T 237). Diazotised sulphanilic acid in alkaline solution reacts with phenol or its derivatives in the following manner:

(*a*) If the *para* position of the phenol is unoccupied the reaction takes place as in I. below.

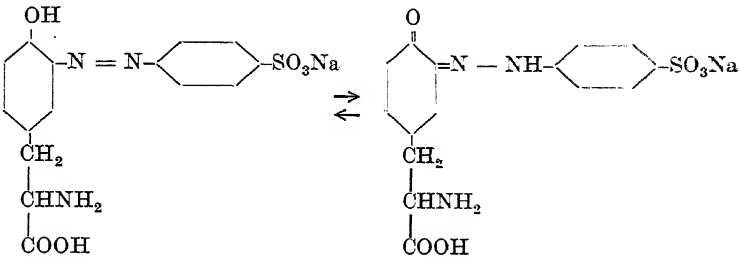
(*b*) If the *para* position is occupied coupling occurs in the *ortho* position relative to the hydroxyl group, as is the case with tyrosine in II.

I.



II. 

The condensation product can exist in both the *enol* (yellow) and *keto* (red) forms. In the presence of sodium hydroxide the yellow phenate compound is formed as above, which, owing to its greater degree of dissociation, passes rapidly into the *quinonoid* form, thus :



Enol form, yellow. *Keto* form, red.

The reagent is prepared by mixing 10 c.c. of a ten per cent. solution of sodium sulphanilate with 5 c.c. of an eight per cent. solution of sodium nitrite, then pouring 2 c.c. of concentrated hydrochloric acid down the side of the vessel, mixing by a gentle rotatory motion and allowing to stand for one minute before use. A weighed quantity of the wool (0·1 grm.) is wetted-out in 15 c.c. of a nine per cent. solution of sodium carbonate, and the reagent added. After exactly 10 minutes the wool is withdrawn, rinsed thoroughly in water and transferred to a test-tube, 4 c.c. of ten per cent. sodium hydroxide solution added and the tube placed in a bath of boiling water for exactly five minutes. The resulting reddish solution is transferred to a graduated flask and diluted to a definite volume. The colour of the solution is then matched with that of a 0·1 per cent. solution of New Acid Brown S or Naphthalene Leather Brown BS (ICI). When 0·1 grm. of wool, treated in this manner and made up to a volume of 25 c.c., gives a solution of the same colour intensity as that of the above dyestuff in 0·1 per cent. solution, the damage is said to be "100 units." The method of calculation used for other values is seen from the following example :

Weight of sample taken, ...	W grms.
Total volume of final solution, ...	25 c.c.
Volume of standard dye solution used, . .	S c.c.

$$\text{Damage} = 100 \times \frac{S}{25} \times \frac{0{\cdot}1}{W} = \frac{S}{W} \times 0{\cdot}4 \text{ units.}$$

The Sulphide Test.—A useful method for the detection of damage produced by alkalis depends upon the fact that treatment of wool with alkalis causes dissolution of part of the sulphur originally present, while part or all of the sulphur remaining is converted into an insoluble substance having the general properties of a sulphide. Hence, if wool damaged by alkalis is immersed in a solution of stannous chloride, acidified with acetic acid, a brown stain is produced in consequence of the formation of stannous sulphide. Undamaged wool does not give this reaction. The depth of colour produced is a rough index of the degree of damage of the wool.

Soluble Nitrogen Test.—One of the most reliable methods of determining the presence or absence of damage in wool consists in determining the percentage of nitrogen which is soluble in a dilute solution of sodium carbonate. Whenever wool is damaged, the protein molecule is rendered unstable and breaks down with the liberation of soluble nitrogenous products when soaked in a cold solution of decinormal sodium carbonate. Undamaged wool on the other hand is only attacked very slowly. A weighed quantity of the sample is soaked for 12 hours in a measured volume of the sodium carbonate solution. The liquid is then filtered and the nitrogen content determined by the Kjeldahl method, or by means of the biuret reaction, which is common to all proteins.

The Biuret Test.—If a little copper sulphate solution be added to a solution of a protein and then excess of sodium hydroxide, the supernatant liquid, after the precipitated copper hydroxide has settled, will have a violet or bluish-violet colour. Approximately quantitative results may be obtained by the method of Becke (*Farber Zeit.*, 1913, **23**, 45, 66):

A series of 10 standards and one blank is prepared, the former by dissolving 1 grm. of wool in sodium hydroxide solution, neutralising with hydrochloric acid and boiling to expel hydrogen sulphide, then making up to one litre. Quantities of 1, 2, 3 . . . 9 and 10 c.c. of this solution are pipetted respectively into ten cylinders and definite quantities of an $N/20$ solution of copper sulphate and normal sodium hydroxide solution added to each cylinder. The blank is then prepared by adding the copper sulphate and sodium hydroxide solutions only to a separate cylinder. All of the cylinders are made up to equal volume. After standing for one hour the colour of the solutions arising from the biuret reaction shows a regular gradation in depth, and permanent standards may be prepared by matching these colours with a suitable dyestuff or recording them with the aid of a Lovibond colorimeter. To determine the diffusible nitrogen at different stages of a process, known volumes of the liquors are neutralised, boiled and treated with the quantities of copper sulphate and sodium hydroxide used in the preparation of the standards; the coloration produced on standing is compared with that of the standards. The diffusible nitrogen can then be calculated in terms of wool substance from the weight of wool and the volume of liquor in the vat or bath.

Sauer's Test for Deterioration of Wool (*Z. angew. Chem.*, 1916, **29**, 424).—This test is based upon the determination of the nitrogen soluble in an alkaline solution of hydrogen peroxide. The procedure consists in treating 0·5 grm. of wool with 40 c.c. of water, 50 c.c. of 1 per cent. hydrogen peroxide solution and 10 c.c. of $N/2$ potassium hydroxide solution for three days at ordinary temperatures. The mixture is then filtered and the nitrogen determined in an aliquot part of the filtrate.

SILK.

The general analysis of raw silk is carried out in the following manner:

Moisture.—About 5 grms. of the sample are weighed in a stoppered weighing

bottle, dried at 100° to 105° C., replaced in the weighing bottle and reweighed. The drying is continued until no further loss of weight is found.

Oil and Fat.—The dry silk is extracted with petroleum ether in a Soxhlet extractor. If much oil be present it should be examined for unsaponifiable matter.

Matter Soluble in Alcohol.—The fat-free silk is placed in a suitable continuous extractor and extracted with alcohol for about four hours. The alcoholic extract is evaporated to dryness and weighed. This residue may consist of soap, glycerol or other alcohol-soluble adulterants.

Matter Soluble in Cold Water.—After extraction with alcohol the silk is covered with cold distilled water and allowed to stand for three hours. The water is then decanted off into a litre flask and the operation repeated until nearly one litre of extract has been obtained. The solution is diluted to exactly one litre and an aliquot part of it evaporated on the water-bath in a flat dish, the residue being dried and weighed. The aqueous extract may contain salts, sugar or other water-soluble bodies, which are identified by qualitative tests.

Silk Gum.—The silk from the foregoing is now dried and weighed. It is then placed in a beaker and boiled gently with a 5 per cent. solution of olive oil soap and a little sodium carbonate solution. When most of the gum has dissolved, usually in about three-quarters of an hour, the silk is removed, squeezed, and boiled for a short time in a fresh soap solution. After this it is washed repeatedly with hot distilled water, dried at 100° to 105° C. and weighed. The difference between the first and second weights gives the silk gum.

True Silk.—The residue is true silk, although it may still contain mineral matter. The latter may be determined by ashing a portion of the residue. If desired, the percentage of silk may be checked by determining the nitrogen by the Kjeldahl process and multiplying the percentage obtained by 5·45.

The following is an example of the figures given by a sample of Italian silk which was obviously adulterated:

Water,	9·23	per cent.
Unsaponifiable oil,	2·40	,,
Saponifiable oil,	2·98	,,
Mineral matter,	2·14	,,
Matter soluble in alcohol,	2·21	,,
Matter soluble in cold water,	2·30	,,
Gum,	20·32	,,
Silk,	58·42	,,

The Analysis of Weighted Silk.

The most accurate method for the determination of the proportion of silk in a weighted sample consists of determining the total nitrogen and multiplying by 5·45. But nitrogenous matters other than silk must be removed first; this may be done in the following way: The weighed sample is boiled for half an hour with a one per cent. solution of sodium carbonate, washed thoroughly with hot water, then digested at 60° C. for half an hour with one per cent. hydrochloric acid and again washed. When Prussian blue is present the treatment must be repeated several times. Prussian blue may be removed also by boiling the sample with a dilute solution of acid potassium oxalate and

washing with water. The washed residue is then treated by the Kjeldahl process.

Utz (*J.S.C.I.*, 1923, 177 A) gave the following method: A sample of the silk is dried and weighed in order to determine *moisture.* The dry residue is boiled for seventy minutes in 600 c.c. of a 0·75 per cent. solution of olive oil soap, washed three times with hot distilled water, dried at 105° C. and weighed. The loss of weight gives the *sericin* present. *Fibroin* is determined by boiling 2 grms. of the sample for two hours in a 2·5 per cent. solution of soap and then in sodium carbonate solution (1·01 sp. gr.) until no more ammonia is given off. The residue is then washed and the *nitrogen* content determined by the Kjeldahl method. The percentage of nitrogen multiplied by 5·45 gives the fibroin and the *weighting materials* are obtained by difference.

When *silicate* or *phosphate of tin* has been used for weighting the silk, it may be determined by the method of Heermann and Frederking (*J.S.C.I.*, 1915, 349), in which a weighed quantity of the sample is digested in a platinum dish with a 2 per cent. solution of hydrofluoric acid on a water-bath for about half an hour. The hydrofluoric acid is poured off and the silk treated with 5 per cent. hydrochloric acid, washed, dried and weighed.

Prussian blue may be determined by the process of Williams and Dreaper (*J.S.C.I.*, 1912, 468 and 1076): A weighed quantity of the sample is distilled with a 10 per cent. solution of sulphuric acid and 0·1 grm. of pure cuprous chloride dissolved in a few drops of concentrated hydrochloric acid. The distillate is collected in sodium hydroxide solution and the hydrocyanic acid determined by titration with silver nitrate. Viehoever and Johns (*J.S.C.I.*, 1915, 351) determine the hydrocyanic acid in the distillate by reconverting it into Prussian blue and matching the colour produced with that of suspensions of Prussian blue made from known quantities of potassium cyanide.

The following standard method for the analysis of weighted silks was devised by Appel for the American Silk Association and is taken from the *Textile Colorist*:

"1. *General.*—(i.) By 'weighting' is meant not only metallic weighting, but all materials other than fibroin present in the finished silk after it has been dried to constant weight in air at 110° C. (ii.) The amount of weighting is expressed in per cent. of the weight of the finished silk after it has been dried as above.

"2. *Sampling.*—(i.) A sample taken for analysis should be representative of the material. It is recommended that a strip measuring from two to four inches wide be taken all the way across the original cloth from selvage to selvage. The sample should weigh from 1 to 5 grms.

"3. *Test for Silicate.*—(i.) A small sample of the silk is ignited, the ash is placed in a platinum crucible, and two drops of concentrated hydrofluoric acid are added. If silicate is present, chemical action accompanied by a considerable amount of heat will be noticed.

"4. *Tin Phosphate-Silicate Weighted Silk.*—(i.) The sample is dried to constant weight in an air oven at 100° C. This is called weight 'A.' (ii.) The dried sample is soaked in 100 times its weight of distilled water at 65° C. for twenty minutes. It is moved about in the water every few minutes during this time in order to ensure thorough penetration of water and extraction of water-soluble materials. It is then rinsed in a fresh portion of distilled water, then in alcohol, and finally in ether, after which it is dried to constant weight, as above (two 25-c.c. portions of alcohol and of ether are usually sufficient). This is called weight 'B.'

$$\frac{(\text{Weight 'A'} - \text{weight 'B'})100}{\text{Weight 'A'}} = \text{'finishing materials' per cent.}$$

(iii.) The sample from which 'finishing material' has been removed is soaked in 100 times its weight of 2 per cent. hydrofluoric acid solution at 65° C. for twenty minutes. It is then rinsed in water and treated with 100 times its weight of 2 per cent. sodium carbonate solution at 65° C. for twenty minutes. It is then rinsed in water, in alcohol, and in ether, and dried to constant weight as before. This is called weight 'C.' (iv.) The sample is then ashed, and the ash weighed—weight 'D.' This ash should not weigh more than one-tenth of the difference between weight 'B' and weight 'C.' If the silk contains a considerable amount of weighting, the treatment given in (iii.) above should be repeated, with fresh solutions, before the sample is ashed, in order to obtain a low ash. A few threads of the silk treated along with the sample and ashed will show the operator whether the weighting has been removed in (iii.) or if the treatment must be repeated.

$$\text{Then } \frac{(\text{Weight `A'} - \text{weight `C'} + \text{weight `D'})100}{\text{Weight `A'}} = \text{`weighting' per cent.}$$

"5. *Tin Phosphate Weighted Silk.*—(i.) The procedure for silk which does not contain silicate is the same as that just given in Section 4, except that the sample from which 'finishing material' has been removed is soaked in 100 times its weight of 4 per cent. hydrochloric acid solution at 55° C. for twenty minutes. This is repeated with a fresh solution. The sample is then rinsed in water and soaked in 100 times its weight of 10 per cent. sodium carbonate solution at 55° C. for twenty minutes. It is then rinsed in water and the hydrochloric treatment repeated. The sample is again rinsed in water, then in alcohol and in ether, and dried to constant weight, as before. This is called weight 'C.'

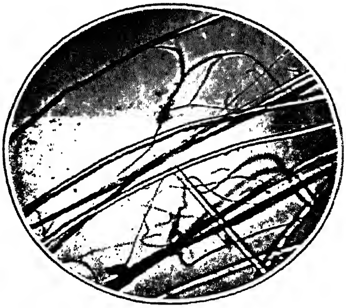


Fig. 48.—Ruptured Silk Fibres.

"6. *Logwood Black Weighted Silk and Silk Weighted with Lead, Zinc or Aluminium Salts.*—(i.) If phosphate is present, the procedure is the same as that given in Section 4, except that the treatment with hydrofluoric acid is preceded by a treatment with 100 times the weight of the sample of 4 per cent. hydrochloric acid solution at 55° C. for twenty minutes, repeated once with a fresh portion of the solution. (ii.) If silicate is not present, the procedure is the same as that given in Section 5."

Uneven dyeing and other troubles are caused often in the case of silk by ruptured fibres or floccons. The identification of these is sometimes of importance. Their appearance under the microscope is illustrated in fig. 48.

ARTIFICIAL SILKS.

The qualitative tests for the different kinds of *rayon* have been described already. The quantitative analysis is not as a rule very helpful, since differences in affinity for dyestuffs, tensile strength, etc., depend chiefly upon physical rather than chemical properties.

A general analysis is carried out in the manner described for cotton. The *copper number* is of importance, but care must be taken in its interpretation, since all forms of regenerated cellulose have a higher number than cotton. The following table is given by Wahl and Rolland (*Rev. Gén. des Matières Colorantes*, 1929, **384**, 1):

Moisture,	10–12 per cent.
Ash,	0·1 –0·56 per cent.
Sulphur—*Viscose*,	0·28–0·4 ,,
Chardonnet,	1·08 ,,
Cuprammonium,	0·20 ,,
Copper number—*Tubise*,	2·98–3·03
Viscose,	0·75–0·95
Celta,	0·79–1·15
Chardonnet,	3·02
Cuprammonium,	0·5 –0·6

The Determination of Sulphur.—About 1 grm. of the finely divided sample is mixed with 2 grms. of magnesia and 1 grm. of sodium carbonate and burnt to an ash. This is washed into a beaker with water, a drop or two of bromine added and the mixture boiled for a few minutes. The liquid is then cooled, acidified with hydrochloric acid, filtered if necessary, and the sulphuric acid determined by means of barium chloride.

Certain special methods of examination have been proposed, which may be described.

Determination of α-Cellulose.—The methods used for the determination of α-cellulose and hemicelluloses have been described under Cotton. (p. 157)

Swelling Properties.—Weltzien (*Textilber*, 1926, **7**, 338) made use of the swelling properties of hydrated cellulose in water and caustic alkalis both for its identification and for the detection of abnormal treatment. The swelling action with sodium hydroxide solution, measured by the weight of the solution absorbed, reaches maxima at 540 per cent. for *viscose* and 850 per cent. for *cuprammonium*, with 10 to 12 per cent. solutions. The swelling diminishes rapidly on either side of the maximum. The swelling is capable of being determined with considerable accuracy except when it is at the maximum, when a solvent action takes place. *Viscose* threads treated with solution of caustic soda show an initial increase in length of about 4 per cent. with concentrations of from 0 to 1 per cent. The extensions then decrease gradually to nil at concentrations of 6 to 7 per cent., the length then diminishing to a minimum at the concentration producing the maximum swelling. Hydrated celluloses treated with caustic soda undergo either no change or a decrease in length (according as the concentration of caustic alkali used was less than or greater than about 6 per cent.) when subsequently washed with water, but a decrease in length (from 3 to 9 per cent.) when subsequently dried. Various forms of cellulose hydrate may be distinguished by their different contractions in length after treatment with caustic soda solution of from 8 to 10 per cent. concentration, the order of shrinkage being

Chardonnet > *viscose* > *cuprammonium*.

Faust and Littmann (*Celluloschem.*, 1926, **7**, 166-168) describe the following method as giving useful information concerning the previous history of a sample: The dry material is treated, by Weltzien's method, with water, then with 4 per

cent. sodium hydroxide, then again with water, and dried, the percentage change in the length of the fibre being determined at each stage. The procedure is then repeated on the same sample. The following figures are given :

	On treatment with Water.	4 per cent. Caustic Soda.	2nd Water treatment.	Drying.
	Per cent.	Per cent.	Per cent.	Per cent.
Normal fibre,	104	103	104	< 100
Fibre strained by loading with 50 grammes,	100·5	98·5	99·2	95·5

In the case of the strained fibre when the process was repeated the results obtained were similar to those for a normal fibre. Thus the effects of abnormal strain which may result in altered dyeing properties or lustre can be corrected by alkaline immersion.

A fibre which had undergone acid treatment, viz., immersion in 0·48 per cent. sulphuric acid, gave the following figures :

	1st Treatment.	Repetition.
	Per cent.	Per cent.
After water treatment,	101·5	106·5
,, alkali treatment,	100·5	106·0
,, 2nd water treatment,	102·0	107·0
,, drying,	94·0	100·0

Dilute hydrochloric acid acted in a similar manner, but acetic acid had very little effect. It may be noted that the effect of acid cannot be counteracted by alkaline treatment, since it produces a fibre which shows abnormally high changes when immersed in water and sodium hydroxide. Excessive bleaching produces also a marked increase in length on treatment with water and alkali which becomes still more marked on repetition, thus :

	1st Treatment.	Repetition.
	Per cent.	Per cent.
Water treatment,	106	108·5
Alkali treatment,	105	108·0
2nd water treatment,	107	109·0
Drying,	97	98·5

It is claimed that this method will not only detect fibres which have undergone severe treatment, but also indicate the nature of the treatment.

Weltzien (*J.S.C.I.*, 1927, B 773) showed that important differences in various types of regenerated celluloses can be detected by extracting with a 9 per cent. solution of sodium hydroxide. A weighed quantity (0·5 grm.) of the sample, chopped up finely, is treated in a stoppered bottle with 30 c.c. of the sodium hydroxide solution at 18°–19° C. for three hours. The mixture is then filtered through a Schott glass filter (size 3/5–7) and the residue pressed, after which it is stirred again with 10 c.c. of the sodium hydroxide solution and allowed to stand for 15 minutes. The undissolved residue is filtered off, sucked dry, washed

with water until free from alkali, dried at 110° C. and weighed. *Cuprammonium* is the most resistant to this treatment, its maximum solubility being 30 per cent., that of *viscose* 40 to 50 per cent., whilst *nitro-silk* is almost completely soluble. The results are affected however by the size of the individual filaments and the temperature of extraction.

Rhodes (*J. Text. Inst.*, 1929, T 55) uses the Ditz test for oxycellulose for the detection of *degraded cellulose*. A modified solution is employed, since tendered viscose dissolves completely in the ordinary Nessler solution. This modified reagent is made by dissolving 100 grms. of mercuric chloride in 500 c.c. of water containing 80 grms. of potassium iodide, adding 5000 c.c. of 3 N sodium hydroxide solution and, after standing over-night, filtering through cotton wool. The test is carried out as follows: Starch and other impurities are removed, after which the sample is immersed in the boiling reagent for one minute. It is then rinsed in warm one per cent. potassium iodide solution and finally in cold water. Over-bleached material, or that containing oxycellulose, is stained much darker than normal material. The test is said to be useful in cases of "barring" in dyeing since "barriness" may be due to the presence of oxycellulose.

Cellulose Acetate.—Since many of the troubles in connection with cellulose acetates are due to saponification of the ester, the most important determinations are (1) regenerated or unchanged cellulose, (2) esterified cellulose. The degree of acetylation is also of interest in some cases.

Unchanged or Regenerated Cellulose.—This may be determined directly in the following manner: About 0·5 grm. of the sample is divided finely and extracted in a small beaker three or four times with small quantities of cuprammonium solution. The undissolved residue is filtered off on a weighed Gooch crucible, washed with dilute hydrochloric acid until free from copper and then with water until the washings contain no acid. The residue of cellulose acetate is dried and weighed.

Determination of the Ester.—A weighed quantity of the sample is extracted in a continuous extractor with acetone for two or three hours. The solvent is then evaporated off and the residue dried and weighed. Or, if the sample be treated in a weighed Schott crucible, the undissolved matter may be weighed and the ester obtained by difference.

Determination of Combined Acetic Acid.—About 1 grm. of the sample is weighed and saponified under an inverted condenser with a solution of alcoholic potassium hydroxide. When saponification is complete, the alcohol is distilled off on a water-bath. The residue is washed into a large distilling flask, acidified with dilute sulphuric acid and distilled with steam until about 600 c.c. of distillate have been collected. The acetic acid in the distillate is then determined by titration with decinormal sodium hydroxide solution in the presence of phenolphthalein.

CHAPTER XII.

OILS.

Sampling.—Liquid oils generally contain undissolved stearin. This must be mixed thoroughly with the oil and sufficient of the sample for the analysis withdrawn at once. Solid fats are sampled by means of an auger or glass tube which reaches to the bottom of the cask. The contents of the tube are melted on a water-bath and mixed.

Determination of Water.—When non-drying oils are being tested, moisture may be determined by drying a little of the sample in a flat-bottomed porcelain dish at 100°–105° C. The oil should be stirred occasionally by means of a glass rod weighed with the dish, to assist in the expulsion of the water. Weighings are made frequently, since most oils increase in weight if heated for a long time in the presence of air.

"Drying" or readily oxidisable oils must be heated in an atmosphere of carbon dioxide, a wide-mouthed glass flask being used for the experiment. If available, a vacuum drying oven may be employed.

When an oil, such as for example a sulphonated oil, contains a high percentage of water the following method is applicable: About 5 grms. of the sample are weighed in a porcelain or nickel dish containing a short glass stirring rod. The dish is placed on a sand bath and heated carefully by means of a small flame until the water begins to boil, the escape being assisted by continually stirring the heated oil. When no more steam is given off and the oil is clear, the dish is at once removed from the sand bath.

Water may be determined also by decomposing it with calcium carbide and measuring the volume of acetylene produced. A nitrometer filled with brine may be used for collecting the acetylene, in a manner similar to that described for the testing of hydrogen peroxide. The oil is weighed in the tube and placed in the decomposition flask, which contains finely powdered calcium carbide. Each cubic centimetre of acetylene at 0° C. and 760 mm. pressure corresponds to 0·00161 grm. of water. The method, however, is not found to be very satisfactory. More reliable results are obtained by mixing the oil with a liquid such as xylene and distilling off and measuring the water. The method is suitable for many materials besides oils, and especially for those which are difficult to dry in an ordinary oven. The organic liquid used must be immiscible with water or saturated with it. Xylene and paraffin satisfy the first condition. A weighed quantity of the sample is placed in a flask of about 250 c.c. capacity and about 100 c.c. of xylene are added. The flask is connected to a small vertical worm condenser and its contents boiled, the distillate being collected in a cylinder which is graduated to 0·1 c.c. When no more water distils over, its volume is read off. The apparatus illustrated in fig. 49, described by Dean and Stark (*Analyst*, 1920, 270), is very convenient.

Insoluble Matter.—This may consist of dirt, nitrogenous organic matter, mineral matter or soaps of calcium and magnesium. A weighed quantity of the oil is extracted in a small flask with petroleum ether and filtered through a

weighed Gooch crucible. When all of the insoluble matter has been transferred to the filter, the latter is washed several times with petroleum ether, dried and weighed. *Insoluble soaps* may be determined by boiling the residue with hydrochloric acid and extracting the liberated fatty acids with ether in a separating funnel.

Melting-point.—Before determining the melting-point of a fat, both dirt and water must be removed. The fat is melted and allowed to stand for some time at a temperature near its melting-point. When the water and dirt have settled, the clear fat is poured off and the last traces of water removed by drying in an oven at a low temperature or by filtering the fat through dried filter paper. When fats are heated for a long time, their melting-points are affected. Rapid cooling of the melted fat also influences the melting-point. The fat should be cooled slowly at atmospheric temperature and the solidified mass allowed to stand for some hours before testing.

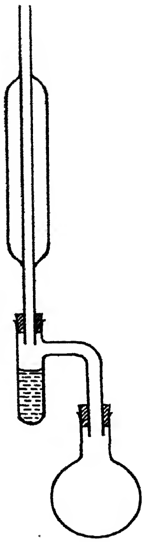


Fig. 49.—Dean and Stark Apparatus.

Many different methods are employed for the determination of the melting-point, the capillary tube method being the simplest. Thin-walled glass tubing is drawn out into capillaries about 10 cm. in length and 1 mm. in diameter and left open at both ends. One end is dipped into the melted fat, which is allowed to rise to a height of about 1 cm. The tube is then removed, the fat allowed to set, and the tube put aside for some hours. The top end is then sealed and the tube attached to a delicate thermometer by means of a rubber band or stuck on to a thin bar of wood by means of sealing wax, the bar being placed across a beaker so that the lower end of the tube containing the fat is immersed in water. When the tube is attached to the thermometer the latter is suspended with the bulb and capillary tube immersed in water in a beaker. The water is heated carefully, with continuous stirring, until the fat melts and rises in the capillary tube.

Specific Gravity.—The *Sprengel tube* (Chapter III) is the most suitable form of apparatus to use in the determination of the specific gravity of an oil. In the case of oils which are turbid or solid at 15·5° C., some higher temperature must be used, such as 100° C.

Viscosity.—The viscosity of an oil is determined in the manner described in Chapter III.

Unsaponifiable Matter and Fatty Acids.—About 5 grms. of the oil are weighed in a small flask, 5 c.c. of a 50 per cent. solution of potassium hydroxide and about 30 c.c. of methylated spirit are added and the contents of the flask boiled gently for about 2 hours in a water-bath, with occasional agitation. The flask is closed by a cork through which passes a glass tube about half an inch in diameter and 24 to 30 inches in length. When saponification is complete the contents of the flask are poured into a separating funnel and the flask rinsed out with distilled water, the washings being added to the contents of the separating funnel. The flask is now washed with about 30 c.c. of petroleum ether, which is then poured into the separator. The latter is closed, shaken with a rotatory motion for a few minutes and allowed to stand until the petroleum ether has separated. If separation is slow, or an emulsion is formed, more alcohol should be added. When the right proportion of the latter is present separation becomes almost instantaneous. The lower layer is drawn off. Since

petroleum ether dissolves soap to a slight extent, especially from an alkaline solution, the petroleum extract is washed several times with distilled water and a little alcohol ; it is then decanted into the flask, which should first be dried and reweighed. The lower liquor is returned to the separator and again extracted with petroleum ether in the same way. The united petroleum ether extracts are then evaporated, dried and weighed. The soap solution and the washings are used for the determination of their *fatty acids* and *oxy-fatty acids*. The alcohol is evaporated off on a water-bath, the soap redissolved in water and washed into the separator. Excess of hydrochloric acid is added and the liberated fatty acids extracted with petroleum ether. Sometimes an insoluble residue remains. This consists of either oxy-fatty acids or rosin acids. The petroleum ether is decanted off into a weighed flask, the solvent evaporated and the residue dried and weighed. The insoluble residue is washed two or three times with petroleum ether and then treated with warm alcohol, which dissolves both *oxy-fatty acids* and *rosin acids*. The solution is filtered if necessary, evaporated to dryness in a platinum or silica dish, and the residue weighed. The acids may contain some *mineral matter*, such as salt. This is determined by burning the residue to an ash and deducting the weight from that obtained in the first weighing. *Rosin acids* are partly dissolved by the petroleum ether. They are detected by the following test: About 1 grm. of the mixed fatty acids is warmed with acetic anhydride in a dry test-tube until a clear solution is obtained. This is poured on to a porcelain plate and allowed to cool. A drop of concentrated sulphuric acid is placed on the plate and allowed to coalesce with the solution of the fatty acids. In the presence of rosin acids a violet colour is produced. The quantitative determination of rosin is described under Soap.

Examination of Unsaponifiable Matter.—The unsaponifiable matter may contain hydrocarbons, rosin or the higher alcohols formed by the saponification of waxes and which are insoluble in petroleum ether. Among these higher alcohols are *cholesterol*, *isocholesterol* and *phytosterol*. The first two are present in animal fats and waxes, whilst phytosterol is a constant constituent of vegetable oils. Hence if phytosterol is present in a reputed animal oil, adulteration with a vegetable oil is established. The identification of these alcohols depends upon the formation of their acetates and determination of the melting-points. The unsaponifiable matter obtained from about 50 grms. of the fat is boiled with a little acetic anhydride for a few minutes and the excess evaporated off on a water-bath. The residue is dissolved in a little hot alcohol and allowed to crystallise. The crystals are washed with cold 95 per cent. alcohol and recrystallised from hot alcohol, after which the melting-point is taken. Cholesterol acetate melts at 114·3°–114·8° C., phytosterol acetate at 125°–137° C. If the melting-point of the crystals is about 114° C., no phytosterol can be present ; if higher, the crystals are recrystallised again. Windhaus (*Analyst*, 1910, 256) based a simple method for the separation of these alcohols upon the fact that they form compounds with digitonin which are insoluble in water, acetone and ether and almost insoluble in 98 per cent. alcohol. Only free alcohols are precipitated in this way, not esters. Kuhn, Bengen and Werwerinke (*Analyst*, 1915, 506) recommended the following method: The mixed fatty acids obtained by saponifying 50 grms. of the fat are treated with 20 c.c. of a one per cent. alcoholic solution of digitonin for one hour at 70° C., the mixture diluted with 20 c.c. of chloroform and filtered. The precipitate is washed with chloroform and ether and dried. It is then acetylated, the acetate crystallised and its melting-point determined as already described.

Lewkowitsch (*Oils, Fats and Waxes*, Vol. I., 379) gives the following method for determining approximately the proportion of alcohols in the unsaponifiable

matter: The unsaponifiable matter is weighed and boiled with twice its weight of acetic anhydride under a reflux condenser. The acetylated mass is then poured into 300 c.c. of boiling water to decompose the excess of acetic anhydride, and when cold the mixture is filtered through a weighed filter, the residue washed with water until free from acid and the filter dried and weighed. From the increase in weight preliminary information may be obtained as to the proportion of alcohols present by consulting the following table:

	Formula.	Melting-point.	Iodine Value.	Acetates.		Increase in Weight on Heating with Acetic Anhydride.
				Saponification Value.	Melting-point.	
Cetyl alcohol, .	$C_{16}H_{34}O$	50° C.	0	197·5	22–23° C.	17·2
Octodecyl alcohol,	$C_{18}H_{38}O$	59° C.	0	180·0	31° C.	15·5
Ceryl alcohol, .	$C_{27}H_{56}O$	79° C.	0	128·1	65° C.	10·6
Myricyl alcohol, .	$C_{30}H_{62}O$	85° C.	0	116·7	70° C.	9·6
Cholesterol, . .	$C_{27}H_{46}O$	148·5° C.	68·3	135·5	114° C.	11·3
*Iso*cholesterol, .	$C_{27}H_{46}O$	137·8° C.	68·3	135·5	...	11·3
Phytosterol, .	$C_{27}H_{46}O$	137·5° C.	68·3	135·5	125·6–137° C.	11·3

Some other information is given (*loc. cit.*) by the behaviour of the unsaponifiable matter with acetic anhydride.

(*a*) If the unsaponifiable matter dissolves completely and no separation takes place on cooling, the presence of *aliphatic alcohols* is indicated.

(*b*) If the unsaponifiable matter dissolves completely and a magma of crystals separates on cooling, the *higher aliphatic alcohols* or *cholesterol* or *phytosterol* are present.

(*c*) If the solution is not homogenous and a clear oily layer floats on the surface, considerable quantities of *hydrocarbons* must be present. At the same time, alcohols (*a*) and (*b*) are not necessarily absent. The lower layer should be separated and examined. The saponification value of their acetates gives information about the nature of the alcohols, and when only one is present serves for its identification.

The Titer of the Fatty Acids.—The *setting-point* of the mixed fatty acids, or "titer," gives valuable information as to the origin of an oil, since this constant does not vary very much in genuine samples. The test is described in dealing with soap.

Free Fatty Acids.—About 2 grms. of the oil are weighed in a flask, 25 c.c. of neutralised spirit added and the flask warmed on a water-bath until the oil (if solid) has melted. Phenolphthalein is then added and decinormal sodium hydroxide solution run in, with constant rotation of the contents of the flask, until a faint pink colour is produced. Each cubic centimetre of decinormal alkali used corresponds to 0·0282 grm. of oleic acid.

Saponification Value.—From 1 to 2 grms. of the oil are weighed into a flask of about 150 c.c. capacity and 25 c.c. of a seminormal alcoholic solution of potassium hydroxide are added, a second 25 c.c. being run simultaneously into another flask to serve as a blank test. The two flasks are covered with watch glasses or connected to air condensers and heated on a water-bath for about an hour, or until saponification is complete. The watch glasses or condensers

are then rinsed down with neutralised spirit, phenolphthalein added to each flask and the unused alkali determined by titration with seminormal hydrochloric acid, the blank test giving the total alkali taken. The *saponification equivalent* is defined as the *number of milligrammes of potassium hydroxide required to saponify one gramme of the fat.*

Ash.—This is determined by burning about 10 grms. of the oil in a silica or platinum dish. If the ash is considerable in quantity and white, it may be desirable to determine the *calcium*, since this will probably be present in the form of calcium soap.

Iodine Value.—After the determination of unsaponifiable matter, the iodine value is by far the most important single test. It measures the proportion of unsaturated fatty acids present in the sample and is expressed as the *amount of iodine absorbed by* 100 *parts of the oil.* A standard solution of iodine is required, two forms of which are in common use, viz., Wij's solution and Hanus' solution. The latter is simpler to prepare and gives reliable results.

Hanus' Solution consists of iodine monobromide dissolved in glacial acetic acid. It may be prepared by dissolving 6·6 grms. of iodine in 500 c.c. of glacial acetic acid by warming the mixture on a water-bath and then adding 1·5 c.c. of bromine. The solution should be kept protected from light.

Wij's Solution.—13 grms. of iodine are dissolved in one litre of glacial acetic acid and the halogen content in terms of sodium thiosulphate is determined. Washed dry chlorine is now passed in until the halogen content is exactly doubled. Another way of making the solution is to dissolve 9·4 grms. of iodine trichloride and 7·2 grms. of iodine separately in warm glacial acetic acid, mix the solutions and dilute to one litre with glacial acetic acid.

The Conference of the *International Union for Pure and Applied Chemistry*, 1928, recommended the following method of preparing the iodine solution: The iodine solution is made by dissolving 9 grms. of iodine trichloride in a litre of glacial acetic acid or in a mixture of 700 c.c. of glacial acetic acid and 300 c.c. of carbon tetrachloride. The strength is determined by adding to 5 c.c. of the mixture 5 c.c. of $N/10$ potassium iodide solution and 30 c.c. of water, titrating with $N/10$ sodium thiosulphate solution in the presence of starch. Powdered iodine (10 grms.) is then added and sufficient brought into solution by agitation to give a halogen concentration of 1·5 times the first value. The solution is filtered and may if desired be diluted with acetic acid until 10 c.c. are nearly equivalent to 20 c.c. of decinormal sodium thiosulphate solution. The addition of carbon tetrachloride to the iodine solution prevents it from solidifying at low temperatures.

Test.—The test is made as follows: Some of the oil is weighed in a small beaker containing a glass tube drawn out to a fine orifice. About 4 drops of the oil (0·1–0·2 grm.) are then introduced into a dry stoppered bottle of about 500 c.c. capacity, the weight of oil taken being determined by difference. A similar dry bottle is taken for the blank test. To each bottle are added 10 c.c. of carbon tetrachloride, and when the oil has dissolved, 20 c.c. of the iodine solution, the stoppers being replaced and the bottles allowed to stand in a dark cupboard for about 4 hours, the contents being agitated occasionally. 20 c.c. of a 10 per cent. solution of potassium iodide are then added to each bottle and, after the iodine has dissolved, 200 c.c. of water. The contents of the bottles are titrated with decinormal sodium thiosulphate solution, starch being added towards the end of the titration. The blank experiment gives the total iodine, and the difference between the two titrations the iodine absorbed by the oil. It is essential that about half of the iodine taken should remain at the end of the experiment.

Separation of the Unsaturated Fatty Acids.—Whilst the iodine value of an oil is an approximate measure of the quantity of unsaturated fatty acids present, it does not permit of their actual separation. In order to effect a separation Varrentrapp's method is employed, which depends on the fact that the lead salts of unsaturated fatty acids are soluble in cold ether, whilst those of the saturated fatty acids are only sparingly soluble. In Lewkowitsch's modification about 4 grms. of the mixed fatty acids, or of the oil, are saponified with 50 c.c. of approximately seminormal alcoholic potassium hydroxide. The soap solution obtained is made slightly acid to phenolphthalein with acetic acid and then carefully neutralised again with alcoholic potassium hydroxide. The solution is then diluted to about 100 c.c. with water, and treated with lead acetate in the following manner: 30 c.c. of a 10 per cent. lead acetate solution are diluted with 150 c.c. of water, heated to the boiling-point and added slowly with constant shaking to the soap solution. The lead soap formed should adhere to the sides of the flask when the mixture is cold. After addition of the lead acetate, the flask is filled with hot water and its contents allowed to cool. The clear liquid is then filtered and any lead soap which remains on the filter is put back into the flask. The residue in the flask is washed with boiling water, which is then allowed to cool before filtering, the lead soaps being put back into the flask again. About 150 c.c. of ether are poured into the flask, which is then corked and shaken to break up the lead soaps. The flask is now attached to a reflux condenser and heated on a water-bath, to dissolve the lead soaps of the unsaturated fatty acids, until the undissolved soaps remain as a fine powder. The mixture is then cooled and filtered through a ribbed filter into a separating funnel, the top of the filter funnel being covered with a clock glass. The insoluble soaps are washed on to the filter by means of ether, using 30–40 c.c. each time. The ether solution in the separating funnel is shaken with excess of hydrochloric acid (1 : 4) and after separation of the lead chloride the lower layer is drawn off. The ether solution is washed with water until free from acid, filtered into a weighed flask, the ether evaporated off and the residue dried and weighed. When fatty acids more unsaturated than oleic acid are present, it is advisable to distil off the ether in a current of dry carbon dioxide or dry hydrogen. The flask is then immersed up to the neck in warm water, which is heated until it boils, to remove the last traces of moisture.

The Acetyl Value.—The presence of *hydroxy-fatty acids* is indicated when the mixed fatty acids are incompletely soluble in petroleum ether. When more accurate information is required the determination of the "acetyl value" must be made. This is defined as *milligrammes of potassium hydroxide required to neutralise the acetic acid obtained when one gramme of the acetylated oil is saponified.* It is, therefore, a measure of the *hydroxyl* groups present in the original oil.

The test consists of two distinct operations: (1) The preparation of the acetylated oil, (2) the determination of the acetic acid. In order to acetylate the oil about 10 grms. of the sample are boiled with 20 to 25 grms. of acetic anhydride in a small flask attached to a vertical condenser. The mixture is then mixed with about 500 c.c. of hot water in a large beaker and boiled for half an hour, a stream of very small bubbles of carbon dioxide being passed through the liquid to prevent bumping. The beaker is then allowed to stand until the oily layer has separated. The water is syphoned off and the boiling repeated three times, or until the last traces of acetic anhydride have been removed. The boiling should not be prolonged after this point has been reached, since it might cause hydrolysis of the acetylated oil. The oil is now filtered through a dry filter paper in a drying oven. About 5 grms. of the dry

acetylated oil are saponified with an excess of alcoholic potassium hydroxide solution as in the determination of the saponification equivalent. The alcohol is evaporated off and the residual soap dissolved in water. Two methods for the determination of the acetic acid may be used. In the first the soap solution is made slightly acid with sulphuric acid and distilled with steam until no more acid comes over, the acetic acid in the distillate being determined by titration. In the second method a volume of standard sulphuric acid exactly equivalent to the alkali used in the saponification is added to the soap solution and the mixture warmed gently until the fatty acids form a clear layer on the surface. These are filtered off through a wet ribbed filter paper and washed with hot water until the washings are no longer acid. The filtrate is then titrated with decinormal sodium hydroxide solution, with phenolphthalein as indicator.

The acetyl value may be deduced also from the saponification value of the oil before and after acetylation. Cook (*J.S.C.I.*, 1922, 299 A) gives the formula

$$A = (S' - S)/(1 - 0{\cdot}00075S),$$

where A is the acetyl value and S and S′ the saponification values before and after acetylation.

The chief difficulty in the process is the washing of the acetylated oil. This may be avoided by the method of André (*Bull. Soc. Chim.*, 1925, 355), which is said to give consistent results. 2 grms. of the oil are heated for an hour with 2 grms. of acetic anhydride and 25 c.c. of xylene (boiling-point 135° C.–138° C.). The excess of acetic anhydride is distilled off by immersing the flask in an oil bath at a temperature of 175° C., this distillation being repeated twice, 25 c.c. of xylene being added each time. A second portion of 2 grms. is treated in the same manner, except that no acetic anhydride is used. The saponification values of both are then determined. The difference between these multiplied by the factor 60/56 (= 1·071) gives the acetyl value.

The *Third French Scientific Commission Report* recommended a comparatively simple method of determining the "*hydroxyl number*" of an oil, which expresses the *number of milligrammes of potassium hydroxide necessary to neutralise the acetic acid contained in the product of acetylating one gramme of the oil.* 2 grms. of the sample are boiled for three-quarters of an hour with 4–6 grms. of acetic anhydride and the excess of acetic anhydride removed by heating the mixture on a water-bath and passing carbon dioxide through the liquid. The residue is cooled to 20° C., a little ether and then 5 c.c. of water added. The mixture is then neutralised exactly with cold decinormal potassium hydroxide solution, phenolphthalein being used as indicator, 50 c.c. of seminormal alcoholic potassium hydroxide solution are added and the mixture saponified for half an hour. The excess of potassium hydroxide is then determined by back-titration. The titration number gives the potassium hydroxide required to saponify the glycerides and the acetic esters. If the saponification value in the case of oils, or the ester number in the case of acid oils, be subtracted, the remainder corresponds to the "hydroxyl" groups present.

Ester Value.—This denotes the *difference between the amount of potassium hydroxide required to neutralise the free fatty acids and the fatty acids combined with glycerol as esters.* If an oil consists entirely of neutral glycerides, its acid value will be nil, and the saponification value indicates the amount of caustic potash required to neutralise the combined fatty acids. When oils contain free fatty acids the saponification value will be the sum of the amounts of caustic potash necessary to neutralise the free fatty acids and those present as glycerides. The difference between these gives the potassium hydroxide required by the neutral fats and this for one gramme of the oil is the "ester value."

Detection of Rancidity.—Rancidity is preceded by the production of *free fatty acids*, but oils which contain free fatty acids are not necessarily rancid. The development of rancidity is accompanied by the formation of *oxy-fatty acids*, *peroxides*, *aldehydes* and *ketones*, particularly *œnanthaldehyde*, $C_6H_{13}CHO$, and oxidation products of glycerol.

Kreis (*J.S.C.I.*, 1903, 575) used sesamé oil for the detection of rancidity, which gives a green colour with aldehydes in the presence of concentrated hydrochloric acid. The sesamé oil was replaced later by ether solutions of resorcinol, phloroglucinol or naphthoresorcinol containing 1 part per 1,000. The fat is shaken with hydrochloric acid (sp. gr. 1·19) together with a little of the reagent. The following colours are obtained :

Resorcinol, ...	Violet.
Phloroglucinol, ...	Red.
Naphthoresorcinol, ...	Green.

Vol Fellenberg (*Chem. Zentr.*, 1925, **96,** 587) uses a reagent consisting of 5 grms. of fuchsin dissolved in 800 c.c. of water, 12 grms. of crystalline sodium sulphite and 100 c.c. of 0·1 *N* hydrochloric acid, diluted to 1 litre, the reagent being kept in the dark. 1 c.c. of the oil dissolved in an equal volume of light petroleum is shaken vigorously with from 1 to 2 c.c. of the reagent for half a minute and examined after 10 minutes. The production of a colour either in the aqueous layer or the oil indicates rancidity.

Rancid fats give reactions for *peroxides*. According to Bullir (*J.S.C.I.*, 1926, B 66), if 1 c.c. of the fat dissolved in 1 c.c. of light petroleum is shaken with 2 c.c. of alcoholic potassium iodide solution, 15 c.c. of water added, the mixture again shaken and the aqueous layer tested by means of starch, a blue colour is developed. For quantitative methods of examination of rancid oils a paper by Taffel and Revis (*J.S.C.I.*, 1931, 87 T) should be referred to.

Detection of β-Naphthol in Oils.—A little of the oil is saponified with alcoholic sodium hydroxide. The alcohol is removed and the soap dissolved in water. Salt is added until the soap is precipitated. The mixture is then filtered and diazotised sulphanilic acid is added to the filtrate. In the presence of β-naphthol an orange colour, due to Orange II., is produced.

Oils Used in the Textile Industries.

The principal oils and fats used in the textile industries are, olive oil, oleic acid, arachis or earth-nut oil, neatsfoot oil, castor oil, tallow and stearin.

When selecting an oil for the lubrication of textile fibres, the chief considerations are (1) the proportion of unsaponifiable oil, (2) freedom from rancidity or crude impurities which would promote the production of rancidity, (3) the absence of drying oils or hydroxy-fatty acids.

In the case of spinning oils the flash-point is also of importance, and also the liability of the oil to spontaneous combustion, due to oxidation. The *flash-point* is determined by the "open" test. About 50 c.c. of the oil are placed in a nickel dish of 75 c.c. capacity. The dish is embedded in sand on a sand bath in such a way that the level of the sand is slightly above that of the oil. The sand bath is then heated gently, the temperature of the oil being observed by means of a delicate thermometer, the bulb of which is immersed in the oil. From time to time the top of a small Bunsen flame is made to impinge momentarily on to the surface of the oil. The temperature at which a slight flash of burning vapour is seen is known as the "flash-point" of the oil. *Liability to combustion* is determined by means of Mackey's Oil Tester. This

apparatus (fig. 50) consists essentially of a cylindrical metal water-bath with a lid through which a thermometer passes and fitted with two tubes, A and B, for the circulation of air in the direction indicated by the arrows. The oil to be tested is distributed carefully throughout pure cotton wool, 14 grms. of the former and 7 grms. of the latter being used. The oiled cotton is placed in the wire gauze cylinder C and packed round the thermometer. The water in the bath is now heated to the boiling-point, the gauze cylinder placed in the bath and the lid fixed by means of the clamp D. The water in the bath is kept boiling and the temperature of the oiled cotton is noted after an hour. If the temperature be above 100° C. the oil is regarded as dangerous, and if the temperature be 150° C. or higher the danger of spontaneous ignition is very great.

In the case of oils used for lubricating yarns in knitting, the following method may be used: 1 grm. of finely divided pure lead is spread in a thin layer over the surface of a small flat-bottomed dish. The dish is weighed, 0·5 c.c. of the oil is distributed as evenly as possible over the lead, and the dish again weighed to obtain the weight of the oil. The dish is then placed in an incubator at a temperature of 20° C. or 37° C. and is weighed at intervals of 24 hours until no further increase of weight is observed. Either the total weight of oxygen absorbed may be determined, or a curve showing the rate of absorption may be constructed.

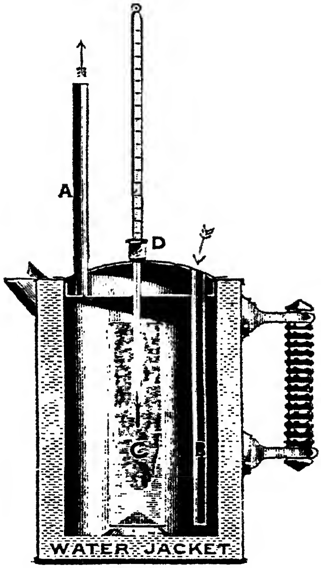


Fig. 50.—Mackey's Oil Tester.

The oils used for knitting and other machines must be readily emulsifiable, free from acidity and oxidised or oxidisable oil, and the flash-point must be high. The following tentative specification for "stainless" mineral oil lubricants for knitting machines has been suggested by an American Committee (*Inst. U.S. Bureau of Standards, Notes*, Jan., 1930): (*a*) The viscosity at 100° F. should be between 70 and 100; (*b*) the flash-point must be not less than 300° F.; (*c*) the colour must pass an accepted standard; (*d*) a clean strip of copper must not become corroded when immersed in the oil for three hours at 212° F.; (*e*) the "neutralisation number" must not exceed 0·10; (*f*) when 10 c.c. of the oil are poured into a test-tube and 5 c.c. of concentrated sulphuric acid are added, no colour should be produced.

Neatsfoot Oil.—Neatsfoot oil is used largely for the preparation of lubricating lather in the knitting of hosiery goods. It is made from the feet of cattle and other animals by boiling with water and skimming off the fat which rises to the surface. The oil has a light yellow colour and as a rule contains a considerable quantity of stearin in a state of suspension. Genuine neatsfoot oil has an iodine value of from 66 to 85 and should not contain more than 0·5 per cent. of unsaponifiable matter nor more than 1 per cent. of free fatty acids. It is adulterated sometimes with mineral oil or vegetable oils such as *cotton seed oil.* The latter, if present in any considerable quantity, would raise the iodine value, but any seed oil would act in the same way. There are, however, qualitative tests by which cotton seed oil may be detected, and of course the

detection of *phytosterol* would prove conclusively the presence of vegetable oil. Provided that the oil has not been heated, 5 per cent. of cotton seed oil may be detected by the Halphen test: About 3 c.c. of the oil are dissolved in an equal volume of amyl alcohol and from 1 to 3 c.c. of a 1 per cent. solution of flowers of sulphur in carbon bisulphide are added. The mixture is heated in a water-bath until the carbon bisulphide has been evaporated off. In the presence of cotton seed oil a deep red colour is produced after heating for from 10 to 15 minutes. The Milliau or Becchi test depends upon the fact that cotton seed oil contains a body which reduces silver nitrate, but it is not applicable to oils which have been heated to a temperature of 240° C. The test is more delicate when applied to the fatty acids. The following method is due to Archbutt and Deeley (*Lubrication and Lubricants*, Griffin, p. 346): About 5 grms. of the oil are saponified with alcoholic potassium hydroxide. The fatty acids are liberated by means of dilute sulphuric acid, extracted with ether, washed with water and dried for 15 minutes on a water-bath. They are then dissolved immediately by pouring 20 c.c. of absolute alcohol into the flask, and the solution is poured into a dry test-tube measuring 8″ by 1″. The contents of the tube are raised to the boiling-point by heating cautiously over a small flame and then, whilst holding the tube over a white tile, 2 c.c. of a 30 per cent. aqueous solution of silver nitrate are added from a pipette. In the presence of 5 per cent. of cotton seed oil a characteristic turbidity is produced at once. If there is no immediate reaction the tube is kept under observation for a minute or two at the boiling-point, and if only two per cent. of cotton seed oil be present a distinct reaction will be developed.

Sesamé oil is detected by the Baudouin reaction. When cane sugar is heated with concentrated hydrochloric acid some furfural is produced, which gives a crimson colour with sesamé oil. The test is made by dissolving 0·1 grm. of cane sugar in 10 c.c. of hydrochloric acid (sp. gr. 1·19), adding 10 c.c. of the oil and shaking the mixture for one minute. If sesamé oil be present the upper layer will acquire a crimson colour. Villavecchia and Fabris (*J.S.C.I.*, 1894, 69) recommended the following modification: 0·1 c.c. of a 2 per cent. solution of furfural is placed in a test-tube and 10 c.c. of hydrochloric acid and 10 c.c. of the oil added. The tube is then corked and shaken. Excess of furfural must be avoided and the hydrochloric acid must be of the correct specific gravity (1·19).

The detection of *arachis oil* will be described under olive oil.

Arachis Oil.—This oil is obtained from the "pea nut" or "earth nut." It is a light coloured oil which is used sometimes for adulterating olive oil, and also for making lubricating lather for hosiery yarns. It is characterised by the presence of about 5 per cent. of arachidic acid, $C_{19}H_{39}COOH$, which melts at 77° C.; lignoceric acid, $C_{23}H_{47}COOH$ (melting-point 80·5° C.) is also present. No oil which does not contain arachidic acid can be arachis oil. *Arachidic acid* may be detected qualitatively by the Bellier test, described under olive oil. The iodine value of arachis oil varies from 85 to 100.

Olive Oil is obtained from the fruit of the olive tree and has a light yellow or greenish colour according to the method of preparation employed. It consists principally of *triolein*, but small quantities of *linolic acid*, $C_{17}H_{31}COOH$, and *arachidic acid* are present also, together with 15 to 25 per cent. of *palmitic acid*, $C_{15}H_{31}COOH$.

The iodine value of genuine olive oil varies between 80 and 85. All the oils used for its adulteration, with the exception of arachis oil, have a higher iodine value and are therefore detected comparatively readily. The presence of *cotton seed oil* or *sesamé oil* may be established by the special tests. *Arachis oil* may be detected by Bellier's test: 1 c.c. of the oil is saponified in a test-tube

with 5 c.c. of alcoholic potassium hydroxide solution (85 grms. in 1 litre of 70 per cent. alcohol) and 1·5 c.c. of acetic acid are added, the concentration of the acid being such as to neutralise exactly the potassium hydroxide used. The tube is cooled to a temperature below 20° C. for 30 minutes. The liquid is then diluted with 50 c.c. of 70 per cent. alcohol (by volume) containing one per cent. by volume of hydrochloric acid and the tube placed in water at 17° C. to 19° C. for an hour. When more than 5 per cent. of arachis oil is present, a precipitate of arachidic acid will be formed. This test is based upon the insolubility of arachidic and lignoceric acids in cold 70 per cent. alcohol. Evers (*Analyst*, 1912, 487) showed, however, that these acids are distinctly soluble and described a modified process of analysis : 5 grms. of the oil are saponified under an inverted condenser for about 5 minutes with 25 c.c. of alcoholic potassium hydroxide solution, made by dissolving 80 grms. of caustic potash in 80 c.c. of water, and diluting the solution to one litre with 90 per cent. alcohol. After saponification, 7·5 c.c. of acetic acid (1 vol. glacial acetic acid to 2 vols. water) are added to the hot soap solution, followed by 100 c.c. of 70 per cent. alcohol (by volume) containing one per cent. by volume of hydrochloric acid, and the mixture is cooled to 12°–14° C. for an hour. The precipitate is filtered off on a small Gooch filter and washed with the 70 per cent. alcohol at a temperature of 17°–19° C., being broken up by means of a loop of platinum wire. The washing is continued until the filtrate no longer gives a turbidity with water, and the volume of the washings is measured. The precipitate is then dissolved in from 25 to 70 c.c. of hot 90 per cent. alcohol, according to its bulk, and the solution cooled to a fixed temperature between 15° and 20° C. If crystals are formed in any quantity, the mixture is allowed to stand at this temperature for from 1 to 3 hours, after which the crystals are filtered off and washed with a measured volume of 90 per cent. alcohol (about half the volume used for the first crystallisation) and finally with 50 c.c. of 70 per cent. alcohol. The crystals are then washed into a flask with ether, the solvent evaporated off and the residue dried at 100° C. and weighed. The melting-point is determined, and if below 71° C. the crystals are recrystallised from 90 per cent. alcohol. When no crystals or only a very small quantity are obtained from 90 per cent. alcohol, sufficient water is added to reduce the concentration to 70 per cent. (31 c.c. of water for each 100 c.c. of 90 per cent. alcohol), and the solution allowed to stand and treated as before. The corrections to be added to the weight of the mixed acids for solubility in 90 and 70 per cent. alcohol are given in the following tables :

Table I.—Solubility of Mixed Arachidic and Lignoceric Acids in 90 per cent. Alcohol.

Weight of Acids in grms.	Correction (grm.) for 100 c.c. of 90 per cent. Alcohol.		
	15° C.	17·5° C.	20° C.
0·9 and over,	0·071	0·081	0·091
0·8,	0·070	0·080	0·091
0·7,	0·069	0·079	0·090
0·6,	0·067	0·077	0·088
0·5,	0·064	0·074	0·085
0·4	0·061	0·070	0·080
0·3,	0·055	0·064	0·074
0·2,	0·048	0·056	0·064
0·1 and less,	0·033	0·039	0·046

Table II.—SOLUBILITY OF MIXED ARACHIDIC AND LIGNOCERIC ACIDS IN 70 PER CENT. ALCOHOL.

Weight of Acids Corrected for 90 per cent. Alcohol.	Correction (grm.) per 100 c.c. of 70 per cent. Alcohol.		
	Melting-point 71° C.	Melting-point 72° C.	Melting-point 73° C.
Above 0·1 grm., . .	0·013	0·008	0·006
0·08–0·10 ,, . .	0·011	0·007	0·006
0·05–0·08 ,, . .	0·009	0·007	0·005
0·02–0·05 ,, . .	0·007	0·006	0·005
Less than 0·02 grm., .	0·006	0·005	0·004
Factor for Conversion of Percentage of Acids to Arachis Oil.			
	17	20	22

Renard's method is also important. It depends upon the fact that lead oleate and the lead salts of liquid fatty acids generally are soluble in ether, whilst those of arachidic and other solid fatty acids are insoluble. The method is used for the separation of the liquid fatty acids of other oils. 10 grms. of the oil are saponified with alcoholic potassium hydroxide, the alcohol evaporated off, the soap rinsed into a separating funnel with hot water and the solution acidified with hydrochloric acid. The liberated fatty acids are extracted with ether and the ether solution evaporated in a wide-mouthed 8 oz. flask. The fatty acids are dried and dissolved by pouring 50 c.c. of rectified spirit (sp. gr. 0·834) into the hot flask. The solution should have a temperature of 110° F. or arachidic and lignoceric acids may separate out. To the hot solution are added 5 c.c. of a 20 per cent. solution of lead acetate, which precipitates the whole of the arachidic and lignoceric acids together with some of the oleic and palmitic acids. The mixture is cooled to about 60° F. and allowed to stand for half an hour. The alcoholic solution is then decanted through a filter paper and the lead soaps extracted with ether until the washings give only a slight colour when shaken in a test-tube with sulphuretted hydrogen water; this indicates that the lead oleate has been removed. The lead soaps should not be washed on the filter, but rinsed back into the flask with ether and digested for a short time, four such treatments generally being sufficient. The lead soaps are now rinsed into a separating funnel with a jet of ether from a wash bottle, any adhering to the paper or flask being decomposed with dilute hydrochloric acid and the products dissolved in ether. Sufficient hydrochloric acid is added to the contents of the separating funnel to decompose the whole of the lead soaps. After the fatty acids have dissolved in the ether the lower layer is run off and the ether solution washed with small quantities of hot water until free from lead chloride. The ether is then distilled off and the fatty acids dried. The dry residue is dissolved by warming with 50 c.c. of 90 per cent. alcohol (sp. gr. 0·834) and the solution cooled to 15° C., when arachidic and lignoceric acids, if present, crystallise out either at once or after standing for a short time. For more accurate determinations the solution is kept for an hour at a temperature of 15° or 20° C. with occasional agitation. The crystals are collected on a small filter, placed over a 100 c.c. cylinder, the filtrate being used to rinse out the flask. The crystals are washed several times with small quantities of 90 per cent. alcohol until the filtrate and washings together make 70 to 80 c.c., the actual volume being measured. Washing is continued with 70 per cent. alcohol until

a few cubic centimetres of the filtrate remain clear when diluted with water in a test-tube. The volume of alcohol used is noted and the crystals are then washed from the filter with hot ether, dried and weighed. Finally the melting-point is determined. The point of incipient fusion should not be below 71° C. The arachis oil may be calculated from the fact that 4·8 parts of arachidic acid represent 100 parts of the oil. The necessary correction should be made for the solubility of arachidic acid in 90 and 70 per cent. alcohol.

Bolton and Williams (*Analyst*, 1930, 5) have published details of a promising method for determining the purity of olive oil. They found that the iodine values of the unsaponifiable matter of oils can be divided into four groups, viz. :

Iodine Value.	Oil.
64–70	Beef fat, butter, lard, kernel oils of palmæ, cocoanut oil, palm kernel oil.
90–96	Cod oil, herring oil, seal oil, whale oil, sardine oil, cocao butter.
117–124	Almond oil, arachis oil, cotton seed oil, grape seed oil, linseed oil, maize oil, palm oil, rape oil, rubber seed oil, sesamé oil, soya oil, sunflower oil, tea-seed oil, tung oil.
197–206	Olive oil.

The *unsaponifiable matter* must be obtained in the following manner: 2–2·5 grms. of the oil are saponified under a reflux condenser with 25 c.c. of $N/2$ alcoholic potash. The solution obtained is titrated with $N/2$ hydrochloric acid, using phenolphthalein as indicator. 5 c.c. of $N/2$ sodium hydroxide solution are then added and the solution extracted three times (or more for fish oils) with 30 to 40 c.c. of petroleum spirit. The combined extracts are washed with 20 c.c. of $N/20$ sodium hydroxide solution, then with 20 c.c. of water, then filtered into a flask, the petroleum spirit evaporated off, and the residue dried and weighed. The following solutions are required for the determination of the iodine value: (*a*) 8 grms. of bromine dissolved in 20 c.c. of glacial acetic acid; (*b*) 10 grms. of concentrated sulphuric acid added gradually to a mixture of 8 grms. of pyridine and 20 c.c. of glacial acetic acid, the mixture being cooled during the addition. Solutions (*a*) and (*b*) are mixed, cooled, and diluted to one litre with glacial acetic acid. The unsaponifiable matter is dissolved in 5 c.c. of chloroform and a measured volume of the reagent (sufficient to leave 50 per cent. excess of bromine) is added to the flask containing the unsaponifiable matter. The mixture is placed in a dark cupboard for 5 minutes, after which 5 c.c. of a 10 per cent. solution of potassium iodide and 40 c.c. of water are added. The liberated iodine is titrated with $N/20$ sodium thiosulphate solution and a blank test is made.

Castor Oil is peculiar in being soluble in alcohol and insoluble in petroleum ether. It has also a very high viscosity and is optically active. It consists chiefly of a triglyceride of ricinoleic acid, $C_{17}H_{32}(OH)COOH$, together with a little triglyceride of hydroxystearic acid. The most important test for its purity is the acetyl value, which should be between 147 and 150. The iodine value is 82 to 90. The specific gravity is unusually high, viz., 0·960 to 0·967.

Linseed Oil.—Linseed oil has marked drying properties and hence should never be used for textile goods. It contains a triglyceride of linolenic acid,

$C_{17}H_{29}COOH$, which is capable of combining with six atoms of iodine or three of oxygen in the presence of moisture, in the latter case trihydroxystearic acid, $C_{17}H_{32}(OH)_3COOH$, being formed. Triglycerides of linolic acid, $C_{17}H_{31}COOH$, and oleic acid, are present also. Linseed oil is characterised by its high iodine value, viz., 175 to 200.

Oleic Acid, $C_{17}H_{33}COOH$.—Commercial oleic acid always contains a certain amount of *stearic acid*, which separates on standing or when the oil is cooled. The percentage of oleic acid may be calculated from the iodine value, since each molecule of this acid combines with two atoms of iodine. When oleic acid is exposed to the action of the air, some of it is converted into dihydroxystearic acid, which is insoluble in petroleum ether. Good samples of oleic acid should contain very little unsaponifiable matter (0·5 per cent.) and be completely soluble in petroleum ether. The iodine value should be about 90.

Sperm Oil.—Sperm oil consists chiefly of an ester of a monohydric alcohol and is therefore a liquid wax. It is a valuable lubricant for light machines. It does not thicken nor does its viscosity fall greatly on heating. Its chief analytical factors are, a low specific gravity, 0·880, low "titer," 11·5° C., and a saponification value of about 124. Its iodine value is from 84 to 90 and its acetyl value 4 to 6. Genuine sperm oil should yield very little or no glycerol when saponified, but owing to the monohydric alcohol being insoluble in water, it will be included with the unsaponifiable matter, which ranges from 39 to 42 per cent. The presence of mineral oil in the unsaponifiable matter is ascertained by determining the acetyl value, melting-point and iodine value of the mixture. For genuine sperm oil these are

Melting-point, ...	23·5°–26·5° C.
Solidifying-point, ...	21·7°–22° C.
Iodine value, ...	64·8–65·2.

The determination of *glycerol* has already been described.

Stearin.—Commercial stearin consists of stearic and palmitic acids, together with a variable but small amount of oleic acid. It should be free from unsaponifiable matter and contain only traces of water and mineral matter. The percentage of oleic acid is calculated from the iodine value, an absorption of 90·07 per cent. of iodine corresponding to 100 per cent. of oleic acid.

The separation of stearic acid, $C_{17}H_{35}COOH$, from palmitic acid, $C_{15}H_{31}COOH$, is effected by the method of Hehner and Mitchell (*Analyst*, 1896, 321), which depends upon the fact that a saturated alcoholic solution of stearic acid is still able to dissolve palmitic acid. Alcohol of specific gravity 0·8183 dissolves 0·155 grm. of stearic acid at 0° C. per 100 c.c. and 1·298 grms. of palmitic acid under the same conditions. A solution of stearic acid is prepared by dissolving 3 grms. of the pure acid in 1,000 c.c. of warm alcohol of specific gravity 0·8183. The solution is placed in a stoppered bottle and kept in ice overnight. After twelve hours the clear solution is syphoned off, without removing the bottle from the ice, by means of a small thistle funnel covered with a piece of fine calico. The funnel is bent twice at right angles and may be attached to a suction bottle, so that the clear liquor can be drawn off with a pump. 0·5–1·0 grm. of the mixed fatty acids is weighed in a flask and dissolved in 100 c.c. of the stearic acid solution. The flask is placed in ice overnight and the mixture agitated next morning, being kept meanwhile in the ice. The alcohol is then filtered off as described above, care being taken to draw off the solution as completely as possible. The undissolved residue in the flask is washed three times with 10 c.c. of the stearic acid solution cooled to 0° C. The crystals adhering to the calico

filter are then washed into the flask without alcohol, the alcohol evaporated off and the residue dried and weighed. The melting-point of the recovered stearic acid should not be much below 68·5° C. A correction of 0·005 grm. is added for the retained stearic acid solution. The palmitic acid is obtained by difference.

Tallow consists of purified beef or mutton fat, its principal constituents being triolein, tristearin and tripalmitin. It has the following characteristics:

Specific gravity,	0·937–0·953
Melting-point,	47°–49° C.
Solidifying-point of fatty acids,	43°–45° C.
Iodine value,	40–45
Acid value,	less than 2
Unsaponifiable matter,	less than 0·5.

Japan Wax is a fat and not a true wax, consisting of triglyceride of palmitic acid, free palmitic acid and other fatty acids. The following are its principal analytical constants:

Specific gravity,	0·975–1·000
Melting-point,	51°–53° C.
Solidifying-point of fatty acids,	58°–60° C.
Iodine value,	4·5–15
Saponification value,	217–222
Acid value,	6–20
Unsaponifiable matter,	0·7–1·5.

Adulterants such as stearic acid or tallow would be indicated by the iodine value or the acid value, whilst true waxes would give a high percentage of unsaponifiable matter.

Carnaüba Wax.—This substance is a true wax containing no glycerides. It is characterised by its high melting-point, viz., 84° C. Its other constants are:

Specific gravity,	0·998
Iodine value,	13
Saponification value,	78–83
Acid value,	2–3
Unsaponifiable matter,	55.

It is adulterated sometimes with Japan wax, ceresin and stearic acid or paraffin wax, but all of these would reduce the melting-point and affect the acid value and unsaponifiable matter. The presence of Japan wax, tallow or other fat would be indicated by the identification of glycerol after saponification.

Sulphonated Oils.—Turkey-red Oil is the most important sulphonated oil. It should emulsify completely when shaken with two volumes of water. Not less than 50 per cent. of fatty matter should be present and only very little unsaponifiable matter. The following qualitative tests are given by Pollak (*J.S.L.T.C.*, 1928, 24): (1) A white emulsion should be formed when 20 c.c. of a 10 per cent. solution of the oil are shaken with 100 c.c. of a 20 per cent. solution of Epsom salt; (2) when 5 or 6 c.c. of normal acid are mixed with 20 c.c. of a 5 per cent. solution of the oil no separation of the oil should take place.

Analysis.—Unsaponifiable matter is determined in the usual manner and *moisture* by the xylene distillation method. The *total fatty matter* is determined

by heating a weighed quantity of the oil with a slight excess of hydrochloric acid and extracting the mixture in a separating funnel with ether.

Unsulphonated Oil.—A weighed quantity of the oil (about 30 grms.) is mixed with water, and 20 c.c. of ammonia solution and 30 c.c. of glycerin are added. The mixture is extracted twice with ether in a separating funnel, the ether solution washed with water, evaporated and the residual fat dried and weighed. A good sample should not contain more than 15 per cent. of unsulphonated oil.

Sulphonated Fatty Acids.—4–5 grms. of the oil are boiled for 40 minutes with 30 c.c. of hydrochloric acid (1 in 5), the flask being shaken frequently during the operation. A screw-stoppered soda water bottle is convenient to use, immersed in boiling water. This converts sulphonic acids into sulphuric acid. The mixture is cooled, transferred to a separating funnel and extracted with ether. The aqueous layer contains the sulphuric acid. It is drawn off and the ether is washed with small quantities of water until free from acid, the washings being added to the sulphuric acid layer. The sulphuric acid is then determined gravimetrically by means of barium chloride. The result (calculated to SO_3) will give the total sulphuric acid, including any present as neutral sulphates. The latter are then determined and deducted. A weighed quantity of the oil is dissolved in ether or chloroform and the solution washed in a separating funnel with small quantities of a saturated solution of pure sodium chloride until the washings give no reaction for sulphates. The united washings are diluted, acidified with hydrochloric acid, and the *sulphates* determined by means of barium chloride.

The method of Hart (*J.S.C.I.*, 1917, 1139) is simpler. The total alkalinity of the oil is determined by titration with seminormal sulphuric acid in the presence of methyl orange. Another weighed portion of the oil (about 8 grms.) is boiled for an hour with 50 c.c. of normal sulphuric acid in a flask connected to a vertical condenser, a few glass beads being added to prevent bumping. The mixture is then cooled, the condenser rinsed down with water, and the acid titrated with normal sodium hydroxide solution in the presence of methyl orange. The addition of 25 c.c. of saturated salt solution and 20 c.c. of ether makes the end-point of the titration more marked. The change in the acidity of the mixture is equal to the difference between the total alkalinity and the acidity due to sodium bisulphate produced in accordance with the equation

$$\begin{aligned} 2\,C_{17}H_{32}OSO_3Na\,.\,COONa + H_2SO_4 + 2\,H_2O \\ = Na_2SO_4 + 2\,NaHSO_4 + 2\,C_{17}H_{32}OH\,.\,COOH. \end{aligned}$$

Since the total alkalinity is known, the combined sulphuric acid corresponding to the sodium bisulphate can be calculated.

Nature of Oil used for Sulphonation.—Loewkowitsch recommends the determination of the acetyl value of the total fatty matter, which should be 125 if pure castor oil has been used.

Alkali.—Ammonia may be determined by distilling the oil with sodium hydroxide, collecting the distillate in a measured volume of decinormal acid and titrating-back the unused acid. Sodium hydroxide is determined by the following method: A weighed quantity of the oil is dissolved in ether and extracted in a separating funnel five times with about 5 c.c. of dilute sulphuric acid. The united washings may contain both ammonium and sodium sulphates. To determine the latter the acid liquid is evaporated and heated carefully until the excess of sulphuric acid is expelled. Some ammonium sulphate is then added and the dish is heated again to expel the ammonium salts. The residual sodium sulphate is then weighed.

Lang (*Ind. Eng. Chem.*, 1928, **20**, 693) recommends the following procedure for the determination of ammonia: To an emulsion of 10–15 grms. of the oil with 50 c.c. of water are added, with continuous shaking, 100 c.c. of 4 per cent. sodium hydroxide solution, followed by 100 c.c. of an 8 per cent. solution of calcium chloride. A gummy calcium soap is precipitated and the ammonia can be distilled off rapidly.

The *French Commission* (*loc. cit.*) gives the following process for the determination of alkali-free and combined fatty acids:

Total Alkali (A).—10 grms. of the oil are weighed into a 250 c.c. Erlenmeyer flask, 150 c.c. of water are added, then 30 grms. of salt and 25 c.c. of ether, this making the end-point of the titration sharper. The mixture is then titrated with seminormal sulphuric acid, 5 c.c. of methyl orange solution (1 in 1,000) being added. The result is calculated to mgms. KOH per gramme (= A).

Alkali less Ammonia, Free and Combined Fatty Acids (C and B).—8 grms. of the oil are weighed into a 500 c.c. Erlenmeyer flask, 50 c.c. of 95 per cent. alcohol are added and the mixture titrated with seminormal sodium hydroxide in the presence of phenolphthalein. The liquid is then boiled for 20 minutes, the loss due to evaporation being made up with water. This is to expel ammonia, and if expulsion is not complete, the boiling should be continued. After boiling, the colour is brought back to red, 150 c.c. of water and 5 c.c. of methyl orange solution added and the titration completed with seminormal sulphuric acid. Then

c.c. $N/2$ H_2SO_4 calculated as mgms. KOH per gramme = fatty acids (B),

c.c. $N/2$ H_2SO_4 — c.c. $N/2$ NaOH calculated as mgms. KOH per gramme = fixed alkali (C),

and $\dfrac{(A - C) \times 1{\cdot}709}{56{\cdot}1}$ = per cent. ammonia.

Water.—In order to determine water, either the distillation method or the direct heating method already described may be used.

The Analysis of Soap.

The general analysis of a soap includes the following determinations: (1) Fatty acids, (2) rosin, if present, (3) combined and uncombined alkali, (4) unsaponified or unsaponifiable oil, (5) sodium silicate and other salts, (6) water.

In addition to making these determinations, it is often desirable to obtain some information about the nature of the oil used in the preparation of the soap, while the measurement of emulsifying power or detergent power is also of use.

The analysis may be carried out in the following manner: First, care must be taken in obtaining a representative sample. A thin slice should be cut right through a bar and the whole of it weighed. If the portion taken for analysis be from the middle of a bar the proportion of water will be too high. On the other hand the outer layers are naturally comparatively dry.

Determination of Moisture.—The direct determination of moisture is not of great importance, since when the other constituents have been determined, it may be obtained by difference. When necessary it may be determined in the

following manner: About 5 grms. of the soap are cut into thin shavings and weighed in a flat-bottomed dish. The dish is placed in an oven heated to about 50° C. for two or three hours. When most of the water has been expelled the temperature of the oven is raised to 105° C. and the dish weighed at intervals until its weight is constant. Drying is accelerated by dissolving the soap in methylated spirit and evaporating on the water-bath. This causes the formation of a thin layer of soap which gives up its water comparatively readily. Water may be determined also by distilling a weighed quantity of the soap with toluene, and collecting and measuring the water which distills over. The apparatus is described under Oils.

Free Fat.—The dry residue obtained from the determination of water is wrapped in fat-free filter paper and extracted with petroleum ether (boiling-point 40°–60° C.) either in a Soxhlet or continuous extractor. Since soap is distinctly soluble in petroleum ether, the solvent containing the dissolved fat is transferred to a separating funnel and washed two or three times with distilled water containing a few drops of alcohol. The residue, after removing the solvent, is dried and weighed. The *unsaponifiable matter* is then determined as already described.

Hoyt (*J.S.C.I.*, 1928, B 273) determines neutral fat in the following manner: 10–15 grms. of the sample are dissolved in hot 94 per cent. alcohol and the solution filtered. A known volume of 0·5 *N* alcoholic potassium hydroxide solution is added to the filtrate and the mixture boiled for 30 minutes under an inverted condenser. The unused alcoholic potash is then determined by titration with 0·5 *N* acid. A blank test is made, as in the determination of the saponification equivalent of an oil. The *neutral fat* is given by the following formula:

$$\text{Neutral fat} = \frac{\text{c.c. } 0{\cdot}5\ N \text{ alkali} \times 28{\cdot}05}{\text{Saponification Equivalent}} \times \frac{100}{\text{Wt. of sample}}.$$

For soap of unknown composition the neutralisation value (mgrms. KOH per grm.) of the separated fatty acids multiplied by 0·97 is approximately the saponification value of the neutral fats from which they are derived.

Fatty Acids and Total Alkali.—About 10 grms. of the soap are weighed and dissolved in hot distilled water. A few drops of methyl orange are added to the solution and normal sulphuric acid run in from a burette until a perceptible red colour is produced. The volume of acid used gives the *total alkali* present. This is calculated to sodium oxide (Na_2O), the factor being 0·031. The beaker is then placed in a water-bath and its contents heated until the fatty acids have melted. The mixture is then poured into a separating funnel, the beaker being rinsed out with hot water. The beaker is rinsed out with 10 c.c. of petroleum ether three times in order to dissolve any residual fatty acids, the petroleum ether being poured into the separating funnel. After cooling, the stopper is inserted and the contents of the separator shaken well to dissolve the fatty acids. The lower layer is drawn off and the petroleum ether poured into a weighed flask. The acid liquor is returned to the separator and again extracted with petroleum ether, this also being poured into the weighed flask. The solvent is then evaporated off and the residual *fatty acids* dried and weighed. It will be noticed frequently that the fatty acids do not dissolve completely in petroleum ether. The insoluble portion may consist of *hydroxy-fatty acids* or *rosin acids*. In such cases the second extraction should be made with ether, the petroleum solution being evaporated off before adding the ether. A mixture of equal volumes of petroleum ether and ether may be used, but it is more convenient to evaporate with the ether separately.

Examination of the Fatty Acids.—*Rosin acids*, if present, will be included with the fatty acids. In order to detect these, about 1 grm. of the mixed fatty acids is warmed in a dry test-tube with a little acetic anhydride until solution is effected. The clear liquid is then poured on to a porcelain plate and allowed to cool. A drop of sulphuric acid is then placed on the plate and allowed to coalesce with the fatty acids. In the presence of rosin a violet coloration is produced. The sulphuric acid should contain 62·5 per cent. of pure acid and may be prepared by mixing 34·7 c.c. of the concentrated acid with 35·7 c.c. of water. *Rosin* is determined quantitatively by Twitchell's method (*J.S.C.I.*, 1891, 804), which depends upon the fact that fatty acids give rise to esters when dissolved in alcohol and treated with hydrochloric acid gas, whereas rosin acids remain unchanged: About 3 grms. of the mixed fatty acids are dissolved in 30 c.c. of absolute alcohol and a rapid stream of hydrochloric acid gas is passed into the solution until no more is dissolved. The solution of the fatty acids should be placed in a beaker and the end of the hydrogen chloride delivery tube attached to a small filter funnel to prevent the solution being sucked back owing to the rapid absorption of the gas. When the solution is saturated with hydrochloric acid the beaker is covered and allowed to stand for an hour to ensure complete esterification. Five volumes of distilled water are then added and the mixture boiled until it becomes clear. The liquid is then transferred to a separating funnel, the beaker rinsed with ether and the whole shaken with this solvent. After allowing time for complete separation, the lower layer is run off and the ether washed with a little water, after which 50 c.c. of a 1 per cent. solution of potassium hydroxide and 5 c.c. of alcohol are added, the separator closed and shaken. The rosin acids will now be dissolved in the lower layer as potassium soaps, the fatty esters remaining in the ether. The solution of the rosin soap is drawn off, decomposed with hydrochloric acid, the liberated rosin acids extracted with ether and weighed. The rosin acids may also be determined by titration with decinormal alkali; if this be done, the mixture of acids and esters after boiling as described above, is run into a separating funnel and extracted with ether as before. The lower layer is drawn off and the ether solution of the esters and rosin acids washed with small quantities of water until no more hydrochloric acid remains. 50 c.c. of alcohol and some phenolphthalein solution are then added and decinormal potassium hydroxide is run in until a faint pink colour is obtained. Assuming that the combining equivalent of rosin acids is 346, the number of cubic centimetres of decinormal alkali used, multiplied by 0·0346, gives the amount of rosin acid in the sample. Twitchell's method does not give very accurate results and small quantities of rosin are indicated sometimes when it is known that none is present.

McNicoll's method (*J. Soc. Chem. Ind.*, 1921, 124 T) gives good results: 2 grms. of the mixed fatty and rosin acids are dissolved in 20 c.c. of a 4 per cent. solution of naphthalene-β-sulphonic acid in pure dry methyl alcohol and heated for 30 minutes under a reflux condenser. The contents of the flask are then cooled and titrated with $N/2$ alcoholic potassium hydroxide solution, phenolphthalein being used as indicator. A blank test is carried out simultaneously with the sulphonic acid titration. The difference between the two titrations gives the rosin acids, the combining weight of which is taken as 346.

The following method is moderately accurate and depends upon the fact that silver salts of rosin acids dissolve in ether, but those of fatty acids are only slightly soluble. 3 grms. of the soap are dissolved in 150 c.c. of hot water and the solution cooled. A slight excess of 10 per cent. silver nitrate solution is then added, the precipitated silver salts filtered off and washed with warm

water until free from silver nitrate. The filter and precipitate are dried at 100° C. and extracted with ether in a Soxhlet extractor for two hours. The ether solution is then transferred to a stoppered cylinder, the flask being rinsed out with ether. Hydrochloric acid is added to liberate the rosin acids and the cylinder shaken until the silver chloride has coagulated. An aliquot part of the ether solution is evaporated and the residue of rosin acids weighed.

Hydroxy-fatty Acids.—When rosin is absent, hydroxy-fatty acids may be detected by treating the mixed fatty acids with petroleum ether. Ordinary fatty acids dissolve, but hydroxy-fatty acids do not, and remain as a brown insoluble precipitate. They may be washed with petroleum ether, dissolved in warm alcohol, the solution evaporated and the acids weighed. The weighed residue is then incinerated and reweighed, the weight of the ash being deducted from that of the crude oxyacids.

Other determinations of importance in connection with the fatty acids are the "saponification" or "combining equivalent," "iodine value" and "titer." The determination of the first two is described under Oils.

The Titer Test.—The melted dry fatty acids are poured into a wide test-tube (6 cm. long and 3·5 cm. wide). The tube is passed through a hole in a cork, the latter being inserted in the mouth of a bottle or boiling tube, a thermometer being placed in the tube containing the fatty acids. The tube is allowed to stand until a few crystals appear. The mass is then stirred once with the thermometer in such a manner that the crystals are mixed with the rest of the fatty acid, but without allowing the thermometer to come in contact with the sides of the test-tube. The temperature will fall for a time after stirring, but finally rise and remain stationary for a short period. The latter temperature is known as the "titer."

Combined and Free Alkali.—The dry soap, after the determination of moisture, or a freshly dried sample, is dissolved in hot industrial methylated spirit, the solution filtered into a 250 c.c. flask and the filter washed with hot alcohol until free from soap. It is preferable, however, to use a continuous extractor. In either case the spirit used should be redistilled in the presence of a little alkali to ensure neutrality. A drop of phenolphthalein is then added to the alcoholic solution. If free caustic alkali is present a pink colour is produced and decinormal acid is run in until this is just discharged. Each cubic centimetre of decinormal acid used is equivalent to 0·004 grm. of sodium hydroxide. The solution is next evaporated until the alcohol has been expelled, the residue redissolved in water and the *combined alkali* determined by titration with normal acid in the presence of methyl orange, the alkali being calculated to sodium oxide, Na_2O. The insoluble residue on the filter contains any sodium carbonate or sodium silicate present in the soap. The filter is washed with hot water and the *soluble alkali* determined by titration with decinormal sulphuric acid, methyl orange being used as indicator. When *sodium silicate* is present it is determined by burning a weighed quantity of the soap to an ash in a platinum dish, acidifying the ash with hydrochloric acid, evaporating to dryness and baking the residue. On extracting with dilute hydrochloric acid the silica remains as an insoluble residue and is filtered off, ignited and weighed.

Schuttig (*J. Soc. Dyers and Col.*, 1920, 185) gives a quicker method than the foregoing. For caustic alkali, 10 grms. of the soap are dissolved in carbon dioxide-free water in a 250 c.c. flask. To the solution are added 25 c.c. of 10 per cent. barium chloride solution. After mixing, the precipitated barium soap is allowed to settle and more barium chloride is added if necessary. The mixture is then cooled, made up to 250 c.c. with carbon dioxide-free water and filtered. The barium hydroxide in the filtrate, which is equivalent to the *caustic*

alkali present in the soap, is determined by titration of an aliquot part of the solution. The *total alkali* is determined in a similar manner, but 40 grms. of sodium chloride are used instead of barium chloride. This is dissolved in carbon dioxide-free water and added slowly to the soap solution with constant shaking. The mixture is made up to 250 c.c. with cold carbon dioxide-free water and filtered. A portion of the filtrate is titrated with decinormal acid in the presence of phenolphthalein, the acid being added until the pink colour disappears and does not reappear on boiling. This gives the *total free alkali*, and the difference between the first and second titrations that present as *carbonate*. It should be noted that the true soap present in a sample is the sum of the combined alkali (as Na_2O) and the fatty anhydrides. The latter may be obtained by multiplying the percentage of fatty acids by 0·97.

Emulsifying Power.—The value of a soap for textile purposes depends largely upon its power of emulsifying oils or fats. This in turn depends upon a low interfacial tension, which may be measured by counting the number of drops formed by a definite volume of the oil when it is allowed to flow from a pipette into a solution of the soap under standard conditions. Donnan's drop-number apparatus may be used. It consists (fig. 51) of a pipette A of about 5 c.c. capacity, provided with a capillary tube B, with a bend at C, drawn off to an orifice at D, which is ground perfectly flat. The pipette is filled with the oil and the outlet D immersed in the soap solution. When the tap is opened the size of the drop which issues from D depends upon (1) the difference in specific gravity of the liquids, (2) the surface tension acting round the circumference at D, which tends to retain the drops. Any decrease in the surface tension shows itself, therefore, in diminished size and increased number of drops formed by the definite volume of liquid flowing from the pipette. If two soap solutions of the same strength be examined, that giving the larger number of drops will have the greater emulsifying power.

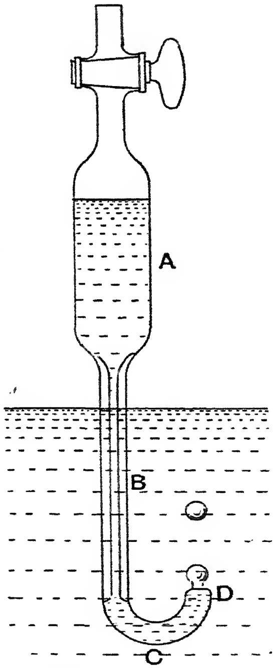


Fig. 51.—Drop-number Apparatus.

Direct Measurement of the Detergent Power.—McBain, Harborne and King (*J.S.C.I.*, 1923, 373 T) proposed a method for the direct determination of the detergent power of a soap which depends upon the colorimetric estimation of the amount of carbon which a solution of the soap will carry through a filter paper. "Auk" carbon black is used and a Whatman No. 31 filter paper 11·3 cm. in diameter. The carbon (1 grm.) is digested with 20 c.c. of the soap solution at a fixed temperature for 23 hours, the mixture then shaken and allowed to stand for another hour. It is then filtered at the temperature of digestion and 10 c.c. of the filtrate diluted to a known volume with alcohol. The colour is then matched by means of a special dye solution consisting of 50 c.c. of Nigrosine solution (0·056 grm. per litre), 20 c.c. of Bismarck Brown (0·0858 grm. per litre) and 100 c.c. of distilled water. The light transmitted by this solution is the same as that of the filtrate from a soap solution having a "carbon number" of 1·19.

The " carbon number " of a soap is given by the formula

$$C = 1{\cdot}19 \frac{l_s}{lw}$$

where l_s and l are the lengths of the columns of standard liquid and filtrate respectively, and w is the weight of the filtrate which has been diluted to 100 c.c. with alcohol.

Hermann (*J.S.C.I.*, 1921, 176 A) measured the detergent power of a soap by an actual washing test. The fabric is artificially soiled with a colloidal indigo paste, or other suitable substance. It is then washed under standard conditions and dried, the degree to which the fabric has been cleansed being judged by its final colour.

CHAPTER XIII.

ORGANIC SOLVENTS.

The principal organic solvents used in the textile industries may be divided into the following groups :

(1) Hydrocarbons, either aliphatic or aromatic.
(2) Hydrogenated hydrocarbons such as tetrahydronaphthalene (*tetralin*).
(3) Hydrogenated phenols, such as *cyclo*hexanol.
(4) Chlorinated hydrocarbons, including carbon tetrachloride, ethylene trichloride, ethane tetrachloride and chlorobenzene.
(5) Ketones, principally acetone.
(6) Alcohols.
(7) Pyridine.

Organic solvents may have to be tested for purity, or identified as such or after separation from a mixture. The general properties of the different types of solvents mentioned above may be considered first.

Hydrocarbons.

Aliphatic hydrocarbons used in textile industry include petroleum spirit, petrol, paraffin oil and paraffin wax. All of these are mixtures of different members of the paraffin series of hydrocarbons, having the general formula, C_nH_{2n+2}.

The aromatic hydrocarbons used are benzene, C_6H_6, toluene, C_7H_8, and xylene, C_8H_{10}. These are procurable in a state of comparative purity. Commercial xylene contains about 85 per cent. of *meta*-xylene, the remainder consisting chiefly of the *ortho-* and *para-* compounds.

Hydrogenated hydrocarbons are derived from benzene and naphthalene and are comparatively pure substances.

The following table gives the boiling points of these solvents :

Petroleum spirit,	40°– 60° C
Petrol,	70°–150° C
Paraffin,	150°–300° C
Benzene,	80·5° C.
Toluene,	110·5° C.
Xylene,	136°–141° C
Tetrahydronaphthalene (*tetralin*),	206° C.

Aliphatic and aromatic hydrocarbons are distinguished from one another by the fact that the former form neither nitro-compounds nor sulphonic acids when treated with nitric or sulphuric acid, respectively. If a hydrocarbon dissolves completely in concentrated sulphuric acid or Nordhausen sulphuric acid, when shaken with it in a separating funnel, it must be of *aromatic* origin. Similarly if when treated with a mixture of nitric and sulphuric acids an oil

or crystalline substance separates when the mixture is diluted largely with water, an *aromatic* hydrocarbon must be present.

Hydrogenated hydrocarbons give rise to nitro-compounds and sulphonic acids, but not so readily as ordinary aromatic hydrocarbons. *Tetralin* may be identified by its boiling point and by Formanek's test, which depends upon the fact that it is coloured red by Algol Red KTH and Lake Red B. Benzene, toluene and xylene act in the same way, but owing to their lower boiling points can be separated easily from tetralin. *Aliphatic* hydrocarbons give no colour with these dyestuffs.

Separation of Aromatic and Aliphatic Hydrocarbons.—The mixture or distillate may either be nitrated or sulphonated, the residue giving the percentage of aliphatic hydrocarbons.

Nitration.—The mixture is dried if necessary over ignited sodium sulphate and filtered. A measured portion of the dry liquid is placed in a stoppered graduated cylinder and shaken with an excess of a mixture of sulphuric acid (4 parts) and nitric acid (3 parts) for 15 minutes, keeping the mixture cool if necessary by means of a stream of cold water. More sulphuric acid is then added and the volume of the aliphatic hydrocarbons read off.

Lunge's modification gives quantitative results. A flask of about 500 c.c. capacity is fitted with a cork through which pass a tap funnel and a long tube to act as an air condenser. From 50 to 100 c.c. of the sample are placed in the flask, the funnel containing a mixture of 150 grms. of nitric acid (sp. gr. 1·4) and 180 to 200 grms. of sulphuric acid (sp. gr. 1·84) which has been cooled after mixing. The acid is allowed to enter the flask in small quantities at a time, the mixture being cooled in water if heat is developed. The flask is shaken continuously during the addition of the acid. After adding all of the acid, and when no further rise of temperature is observed, the flask is connected to a reflux condenser and heated gently on a water-bath for about 60 minutes to complete the reaction. The mixture is then cooled, poured into a separating funnel, and any nitrobenzene which separates is drawn off. The acid layer is poured into a large excess of cold water. Any more nitrobenzene which separates is drawn off and added to the first portion. The crude nitrobenzene is washed in a separating funnel with dilute sodium hydroxide solution and then with water. It is next dissolved in ether, dried with potassium carbonate and distilled until a temperature of 150° C. is reached (nitrobenzene boils at 209° C.). The distillate is nitrated again and treated as before. Finally the nitrobenzene is collected, dried and weighed. Its weight multiplied by 0·63 gives the original *benzene.*

Sulphonation Method.—The dried liquid is placed in a separating funnel and shaken with fuming sulphuric acid, the mixture being kept cool. After allowing the acid to separate, it is drawn off and the process repeated until only a faint colour is produced. The residue is then measured or weighed.

Heilingötter (*Chem. Ztg.*, 1929, **53**, 79) gives the following method: 25 c.c. of the sample are shaken violently in a graduated vessel with 50 c.c. of fuming sulphuric acid (4 to 5 per cent. SO_3). If the temperature rises to 50° C. shaking is stopped and the mixture cooled. When no further heat is developed sulphonation is complete. Sufficient sulphuric acid is then added to bring the contents of the vessel back to the zero mark and the volume of the residue is read off. An elongated graduated separating funnel may be employed with advantage.

Olefines.—Cracked spirits may contain olefines which would also be removed by nitration or sulphonation. When treated with sulphuric acid they absorb the acid rapidly, with the formation of sulphuric esters of the form $RHSO_4$.

Olefines also combine directly with hydrobromic acid, hydrochloric acid and hydriodic acid, and are oxidised readily by potassium permanganate to compounds containing hydroxyl groups. They react very vigorously with bromine, forming addition compounds, accompanied by the disappearance of the colour of the bromine. Other hydrocarbons react slowly with bromine, hydrobromic acid being evolved.

Hydrogenated Phenols.

Hydrogenated phenol or *cyclo*hexanol is sold under the name of *hexalin*. When cresol is hydrogenated a mixture of the three isomeric methyl*cyclo*hexanols is obtained which is put upon the market as *methylhexalin*. These products are viscous liquids with a characteristic camphor-like odour and are free from unchanged phenol or cresol. They are very slightly soluble in water, but miscible in all proportions with benzene, chlorinated hydrocarbons, aniline and turpentine. They have the following constants:

	Sp. Gr. at 15° C.	Boiling Point.	Flash Point.	Refractive Index.	Acetyl Value.
Hexalin, . .	0·945–0·949	155°–160° C.	68° C.	1·4680	561
Methylhexalin, .	0·930	160°–180° C.	68° C.	1·4635	492

Cyclohexanol (*Hexalin*), $C_6H_{11}OH$, is a viscous, colourless liquid, which has a characteristic odour and boils at 160° C. It is lighter than water (sp. gr. 0·94) and only slightly soluble in it. It is miscible with many organic solvents and with a solution of soap in water. When a mixed solvent is under examination the *cyclo*hexanol should be looked for in the fraction distilling between 150° and 160° C. It is not easy to identify, but the following tests may be used:

(1) Since it contains an alcoholic hydroxyl group, *hexalin* reacts with acetyl chloride, acetic anhydride and benzoyl chloride to form esters. The *benzoyl compound* may be obtained in the following manner: The liquid is treated with benzoyl chloride in the presence of sufficient sodium hydroxide solution to keep the reaction mixture faintly alkaline; the reaction may be assisted by attaching the flask to a reflux condenser and warming it gently. The benzoyl compound, $C_6H_{11}O.OCC_6H_5$, separates as an oil. The mixture is washed in a separating funnel with water until the excess of alkali and most of the sodium chloride have been removed. It is then steam-distilled to remove unchanged hexalin, after which the ester is extracted with ether. The ether solution is washed with a very dilute solution of sodium hydroxide to remove free benzoic acid, if present, the washing being repeated until the lower layer remains alkaline. The ether is then removed by evaporation. The benzoyl compound boils at about 220° C., but decomposes when distilled. It is saponified when boiled with alcoholic potassium hydroxide solution, with the formation of potassium benzoate and *cyclo*hexanol.

The foregoing process is troublesome since *cyclo*hexanol is not benzoylated readily under the usual conditions. If, however, dry pyridine is added to the reaction mixture, the reaction takes place very quickly. The solvent containing the *cyclo*hexanol is mixed with the pyridine and the benzoyl chloride added in small quantities. When no more heat is developed the mixture is warmed on a water-bath for a short time to complete the reaction. The excess of pyridine

is removed by washing or by distillation and any unchanged *cyclo*hexanol by distillation with steam.

(2) *Cyclo*hexanol, like other alcohols, reacts with metallic sodium to form an alcoholate, thus:

$$C_6H_{11}OH + Na = C_6H_{11}ONa + H.$$

This reaction may be utilised for the separation of hexalin from the fraction of a distillate which might contain it. The portion collected between 150° and 160° C. is diluted with dry petroleum ether and small pieces of clean sodium are added until no more hydrogen is given off. The precipitated alcoholate is collected and washed with petroleum ether. It may then be treated with benzoyl chloride or decomposed with water, in the latter case the *cyclo*hexanol being regenerated.

Determination of Cyclohexanol.—*Cyclo*hexanol may be determined by converting it into its acetate, as in the case of glycerol, which is described in Chapter XIV.

Chlorinated Hydrocarbons.

The chlorinated hydrocarbons are derived chiefly from ethane and ethylene. They have a characteristic odour like that of chloroform, and their vapours have anaesthetic properties. They are all non-inflammable and heavier than water. The principal commercial examples are *carbon tetrachloride* and *trichlorethylene,* which have comparatively low boiling-points. Carbon tetrachloride, CCl_4, has a specific gravity of 1·631 at 15° C. and boils at 76° C. Trichlorethylene, C_2HCl_3, boils at 87° C. and has a specific gravity of 1·471 at 15° C. The following table gives the specific gravities and boiling-points of other members of the group.

	Formula.	Boiling Point.	Specific Gravity at 15° C.
Dichlorethylene, . . .	$C_2H_2Cl_2$	52° C.	1·278
Perchlorethylene, . .	C_2Cl_4	119° C.	1·624
sym-Tetrachlorethane, . .	$C_2H_2Cl_4$	144° C.	1·601
Pentachlorethane, . .	C_2HCl_5	159° C.	1·685
Hexachlorethane, . .	C_2Cl_6	185° C.	2·090
Chlorobenzene, . . .	C_6H_5Cl	132° C.	1·106 (20°)

The chlorinated hydrocarbons may be identified by their specific gravities, and by the fact that they contain chlorine, which may be identified by the tests described in Chapter V.

Acetone, CH_3COCH_3.

Pure acetone is a colourless liquid, having a specific gravity of 0·796–0·801 at 15° C., and a characteristic odour. It boils at 56·1° C., is miscible with water in all proportions and also with common organic solvents. It is insoluble in a strong aqueous solution of calcium chloride.

Commercial acetone may contain methylethyl ketone, $CH_3COC_2H_5$, methyl alcohol or methyl acetate. ***Methyl ethyl ketone*** has a specific gravity of 0·810 to 0·815 at 15° C. It is miscible with benzene and with three volumes of water. When distilled, about 95 per cent. comes over between 70° C. and 81° C.

Both acetone and methyl ethyl ketone are obtained from the products of

the distillation of wood. After these have been separated, the fraction distilling between 140° C. and 160° C. is known as "light acetone oil" and a second fraction collected between 160° C. and 220° C. as "heavy acetone oil." These oils, are, however, of little use as solvents.

Qualitative Tests for Acetone.—(1) It gives a positive reaction with *Schiff's reagent*, but the colour takes some time to develop, whilst in the case of aldehydes it develops rapidly.

(2) A cold saturated solution of *sodium bisulphite* gives a crystalline precipitate when shaken with acetone. The precipitate has the composition $(CH_3)_2C{<}^{OH}_{SO_3Na}$. It is soluble in water and is decomposed by dilute mineral acids with the liberation of acetone.

(3) When 20 drops of a mixture of 10 c.c. of 10 per cent. acetic acid and 10 c.c. of a 10 per cent. solution of *sodium nitroprusside* are added to a solution of acetone, and, after mixing, a little concentrated ammonia solution is poured down the side of the test tube, a purple ring is formed at the junction of the two liquids.

(4) *Frommer's test.*—Acetone condenses with salicyl aldehyde in the presence of sodium hydroxide to form di*ortho*hydroxydistyryl ketone, which has a red colour. 10 c.c. of the aqueous solution containing acetone are treated with 1 grm. of solid potassium hydroxide and 10 drops of a 10 per cent. solution of salicyl aldehyde in alcohol are added without waiting for the potassium hydroxide to dissolve. The mixture is then heated to 70° C. When acetone is present a purple-red zone appears at the junction of the two liquids.

(5) *Adams-Nicholls Test.*—Acetone condenses with *o*-nitrobenzaldehyde in the presence of sodium hydroxide to form indigo, thus:

$$2\,C_6H_4{<}^{NO_2}_{CHO} + 2\,CH_3\,CO\,CH_3$$

$$= C_6H_4{<}^{NH}_{CO}{>}C = C{<}^{HN}_{OC}{>}C_6H_4 + 2\,CH_3COOH + 2\,H_2O.$$

The indigo separates almost at once as a flocculent precipitate and its appearance is conclusive proof of the presence of acetone.

Determination of Acetone.—In the presence of water or alcohol, acetone may be determined by adding twice its volume of saturated calcium chloride solution and measuring the volume of the separated acetone. It is better to dissolve solid calcium chloride in the liquid.

Messinger's Iodometric Method.—A measured volume of an aqueous solution of the acetone, containing from 30 to 40 milligrammes of the ketone, is added to 50 c.c. of normal sodium hydroxide solution in a stoppered bottle. After five minutes, about 20 per cent. excess of decinormal iodine solution is run in, the mixture being shaken continuously meanwhile. The bottle is then closed, and after standing for 25 minutes, 25 c.c. of 2 *N* sulphuric acid are added to neutralise the sodium hydroxide, and an excess of 0·3 to 0·4 c.c. of the acid introduced. The liberated iodine is determined by titration with decinormal sodium thiosulphate solution. (1 c.c. *N*/10 iodine ≡ 0·967 mgm. acetone.)

Method of Adams and Nicholls.—The qualitative test described above may be used for the colorimetric determination of acetone. A volume of the solution containing not more than 0·2 grm. of acetone is diluted to 10 c.c. with water,

and 1 c.c. of a one per cent. solution of *o*-nitrobenzaldehyde in 50 per cent. ethyl alcohol is added. After mixing, 0·5 c.c. of a 30 per cent. solution of sodium hydroxide is added and the mixture allowed to stand for about 15 minutes, avoiding exposure to strong daylight. The colour produced is compared with that obtained with a series of standards prepared simultaneously and containing from 0 to 20 mgms. of acetone.

Method of Jonescu, Spirescu and Popescu.—10 c.c. of approximately 0·5 per cent. acetone solution are mixed with 10 c.c. of 50 per cent. sulphuric acid, 10 c.c. of mercuric sulphate solution (50 grms. of mercuric oxide dissolved in 200 grms. of sulphuric acid and diluted to 1 litre) and 100 c.c. of water, and the mixture boiled under a reflux condenser for 20 mins.; the precipitate formed is collected on a filter, washed with 200 c.c. of water, then transferred to a flask and dissolved by heating with a mixture of sulphuric acid, 2 parts, and nitric acid, 1 part. A few drops of permanganate solution are added to destroy nitrous compounds, the solution is diluted to 100 c.c., 12 drops of sodium nitroprusside solution are added, and the turbid mixture is titrated with N/10 sodium chloride solution; the disappearance of the turbidity denotes the end-point of the titration. Each c.c. of the sodium chloride solution ≡ 0·0029 grm. of acetone.

Ethyl Alcohol.

Ethyl alcohol is detected by the *iodoform test*, but acetone and acetaldehyde give positive reactions also; these can, however, be removed from the solution with sodium bisulphite. A few drops of a 10 per cent. solution of potassium hydroxide are added to 10 c.c. of the alcoholic liquid and the mixture warmed to 50° C. A strong solution of iodine in potassium iodide is added drop by drop until a permanent colour is produced, which is then just discharged with a very dilute solution of potassium hydroxide. The mixture is allowed to stand. Yellow crystals of iodoform are deposited. These may be identified by their smell and melting-point, 120° C.

Alcohol may be detected in the presence of petroleum spirit by warming the liquid with aniline, which dissolves, but separates again on cooling. It may be determined (Formanek, *Chem. Ztg.*, 1928, **325,** 346) by shaking 100 c.c. of the liquid with 150 c.c. of water coloured with fuchsin and measuring the colourless layer, which represents the constituents other than alcohol. Ethyl alcohol can be identified by the formation of ethyl benzoate (boiling-point 213° C.).

Alcohol can be removed from solvents which are insoluble in water by washing with water in a separating funnel or by using calcium chloride solution. The following method for the examination of liquids containing alcohol, such as motor fuels, is given by Noll (*Z. Spiritusind.*, 1929, **52,** 242, 247): To 10 c.c. of the liquid in a flask graduated from 100 to 110 c.c., calcium chloride solution (dens. 1·3) is added and the mixture shaken for 15 minutes, then being made up to 110 c.c. with the calcium chloride solution. The volume of the hydrocarbons is measured from the graduations on the neck of the flask and the alcohol obtained by difference.

According to Formanek (*loc. cit.*) Aniline Blue 2 B colours alcohol, aldehydes and ketones a deep blue, but is completely insoluble in water, benzene, ether and petroleum products.

The quantitative determination of ethyl alcohol is carried out in the following manner: If the liquid is acid or alkaline it is treated with sodium hydroxide or dilute sulphuric acid respectively. The alcohol is then removed by careful

distillation. The distillate is made up to a definite volume with distilled water and its specific gravity determined. The specific gravity of mixtures of water and alcohol in all proportions is known and hence the percentage of alcohol in the distillate can be found by reference to published tables.

Methyl Alcohol.

Methyl alcohol has a boiling-point of 67·4° C. Its detection depends upon the fact that it is oxidised readily to *formaldehyde*, which can be detected by means of Schiff's reagent or by other tests given in Chapter XIV. The conditions of oxidation are adjusted so that ethyl alcohol, if present, is not simultaneously oxidised to acetaldehyde. The test can be made quantitative if conducted under defined conditions. The procedure is as follows (Jones, *Analyst*, 1915, 218):

The solutions required are

(1) A 2 per cent. solution of potassium permanganate.

(2) A cold saturated aqueous solution of oxalic acid.

(3) Schiff's reagent, made by dissolving 0·2 grm. of Magenta base in 10 c.c. of a freshly prepared cold saturated solution of sulphur dioxide and after 24 hours diluting the solution to 200 c.c. with cold water.

The liquid to be tested is purified, if necessary, by distillation, and diluted with water or ethyl alcohol until it contains 10 per cent. by volume of total alcohol. To 5 c.c. are then added 2·5 c.c. of the permanganate solution and 0·2 c.c. of concentrated sulphuric acid. When the reaction has proceeded for 3 minutes, 0·5 c.c. of the oxalic acid solution is added and then 1 c.c. of concentrated sulphuric acid, after which the liquid is well mixed and treated with 5 c.c. of Schiff's reagent. A violet colour is developed in a few minutes, the depth of which gives an approximate idea of the quantity of methyl alcohol present. If a deep colour is produced, the original liquid is diluted further and a fresh test is made side by side with standards which may contain 0·001 to 0·004 grm. of methyl alcohol in 5 c.c. of 10 per cent. ethyl alcohol. The conditions described must be observed carefully. If too much acid is used in the oxidation, formaldehyde will be produced from ethyl alcohol, whilst if less than 1 c.c. of acid is added in the second part of the test, any acetaldehyde present will give a colour with Schiff's reagent; on the other hand too much acid reduces the sensitiveness of the reaction.

Schryver and Wood's Test.—Ammonium persulphate is used as the oxidising agent: 10 c.c. of the alcoholic liquid are diluted with 50 c.c. of water and 5 c.c. of the diluted mixture are treated with 5 c.c. of a one per cent. solution of ammonium persulphate in a test-tube provided with an air condenser. The contents of the tube are heated for 10 minutes on a bath containing boiling water. 1 c.c. of the solution is then mixed with 1 c.c. of a one per cent. solution of phenylhydrazine hydrochloride and heated as before for 5 minutes. The mixture is then cooled and 1 c.c. of a 2·5 per cent. solution of potassium ferricyanide and 3 c.c. of concentrated hydrochloric acid are added. A pink or red colour indicates methyl alcohol. (*Analyst*, 1920, 164.)

Pyridine, C_5H_5N.

Pure pyridine is a colourless liquid which has a specific gravity of 1·003, boils at 115° C., and has a very characteristic smell. It dissolves in water in all

proportions and is also soluble in alcohol, ether, benzene, chloroform and petroleum ether. It is precipitated from its aqueous solutions by adding brine or strong caustic alkalis. Pyridine has strong basic properties and forms stable salts with strong acids, *e.g.*, pyridine hydrochloride, $C_5H_5N \cdot HCl$, pyridine sulphate, $(C_5H_5N)_2 \cdot H_2SO_4$. When these salts are treated with an alkali the pyridine is liberated. Pyridine is attacked slowly by concentrated sulphuric acid with the formation of a sulphonic acid, $C_5H_4(SO_3H)N$. It also gives halogen substitution products such as C_5H_4BrN. When reduced with nascent hydrogen (*e.g.*, alcohol and sodium), piperidine or hexahydropyridine is formed:

$$C_5H_5N + 6\,H = C_5H_{11}N.$$

This is a colourless liquid, smelling like pepper, with a boiling-point of 106° C. Like pyridine it is soluble in water and has basic properties.

The Detection of Pyridine.—*Pyridine platinochloride*, $(C_5H_5N)_2 \cdot PtCl_4$, is a characteristic salt. When platinum chloride is added to an aqueous solution of pyridine hydrochloride, an orange-yellow precipitate, $(C_5H_5N)_2 \cdot H_2PtCl_6$, is formed, which crystallises as needles. This is soluble in boiling water, but when the solution is boiled for some time, a sparingly soluble yellow precipitate, $(C_5H_5N)_2 \cdot PtCl_4$, is produced, which, when treated with sodium hydroxide, gives the smell of pyridine. *Pyridine picrate*, $C_5H_5N \cdot C_6H_2(NO_2)_3OH$, is thrown down in the form of yellow needles when a solution of pyridine is neutralised with picric acid, or when one containing pyridine hydrochloride is treated with sodium picrate; the precipitate is not formed in dilute solutions and solutions should be concentrated before making the test; the melting-point of the salt is 162° C. Pyridine forms *double salts* with many metals, such as *zinc, cadmium* and *mercury*. When a solution of *mercuric iodide* is added to one containing pyridine, a white precipitate is produced, which dissolves when the mixture is warmed and crystallises out in the form of needles on cooling; this reaction is very delicate, being capable of detecting one part of pyridine in 1,000 of water. Similar double compounds are formed when a solution of either *zinc chloride* or *cadmium chloride* is added to one containing pyridine hydrochloride, the compositions being represented by the formulae $ZnCl_2 \cdot (C_5H_5N)_2$ and $CdCl_2 \cdot (C_5H_5N)_2$.

Lehner (*Chem. Zeit.*, 1922, **46**, 877) gives the following test which is said to detect one part of pyridine in 350,000. It depends upon the fact that when pyridine is treated with aniline and cyanogen bromide, *a-anilidophenyldihydropyridine bromide* is formed. When an aqueous solution of pyridine is mixed with one drop of aniline and a trace of fresh cyanogen bromide, a red coloration and a crystalline precipitate appear immediately.

Pyridine may be extracted from its aqueous solutions by means of ether if the liquid be first treated with a large quantity of sodium hydroxide. It shows an alkaline reaction towards methyl orange but has no action on phenolphthalein; it can be titrated by means of standard acid, 1 c.c. of normal sulphuric acid being equivalent to 0·079 grm. of the base. Commercial pyridine has a yellow or brownish colour; in addition to pyridine it may contain *picoline*, $C_5H_4N \cdot CH_3$, *pyrrole*, C_4H_5N, and *ammonia*; *water* may be present also.

Determination.—When ammonia is absent pyridine may be determined by titration with standard sulphuric acid in the presence of methyl orange. When it contains ammonia a little phenolphthalein is added to the aqueous solution and the acid run in carefully until the pink colour is just discharged. Methyl orange is then added and the titration completed. Ferric chloride is used sometimes as indicator instead of methyl orange, but according to Bayer (*Analyst*,

1912, 413) ferric thiocyanate is the best indicator. The solution is acidified with decinormal hydrochloric acid, ferric chloride and ammonium thiocyanate are added, and then decinormal sodium hydroxide until the red-brown liquid becomes quite colourless. When ammonia is present the pyridine is first neutralised with decinormal sulphuric acid and distilled. The whole of the pyridine, with very little ammonia, passes over with the first third of the distillate. Any ammonia present is titrated with decinormal acid, excess of acid is then added and the pyridine determined as before. When ferric chloride is used as indicator the acid is run in until the precipitated ferric hydroxide is just dissolved.

Ammonia in pyridine may be determined accurately by converting it into magnesium ammonium phosphate, which is filtered off, washed with 2 per cent. ammonia solution, ignited and weighed as pyrophosphate. For the determination of pyridine in ammonia solution the method of Houghton (*J. Ind. Eng. Chem.*, 1909, **1**, 668) may be employed. A mixture of 100 c.c. of the ammonia solution and 150 c.c. of water is neutralised with dilute (1 : 3) sulphuric acid, with methyl orange as indicator, and then made alkaline with 5 c.c. of decinormal sodium hydroxide solution and distilled. The vapours are conducted through sodium hypobromite solution and then into decinormal acid. The hypobromite solution, which is prepared by adding 25 c.c. of bromine to 100 grms. of sodium hydroxide dissolved in 100 c.c. of water, decomposes the ammonia with the liberation of nitrogen, leaving the pyridine unchanged, which is then absorbed by the acid. If the latter be titrated, each cubic centimetre which has been neutralised is equivalent to 0·0079 grm. of pyridine.

Delepine and Sornet (*Analyst*, 1911, 508) treat the distillate containing pyridine and ammonia and a slight excess of hydrochloric acid with mercuric chloride, sodium carbonate and sodium hydroxide, in the order named. The ammonia gives a precipitate of mercurammines, which is filtered off and washed with a solution of 10 grms. of sodium carbonate and 10 grms. of sodium hydroxide per litre. The precipitate is then distilled in the presence of a solution of sodium thiosulphate into an excess of hydrochloric acid. The solution is evaporated and the residual ammonium chloride dried at 105° C. and weighed.

Another method, by Harvey and Sparks (*J.S.C.I.*, 1918, 41 T), depends upon the fact that pyridine bases are precipitated as periodides by an excess of iodine from an acid solution of ammonium salts. After precipitation and washing, the periodides are treated with a small excess of sodium thiosulphate, the mixture neutralised with $N/10$ sodium hydroxide in the presence of methyl orange and then titrated in the presence of phenolphthalein. (1 c.c. $N/10$ $NaOH \equiv 0{\cdot}0079$ grm. pyridine.)

The following directions for the testing of pyridine have been formulated by the *German Customs' Board* (*Chem. Zeit.*, 1913, **37**, 1035) :

" *Colour*.—The colour should not be darker than that of a freshly prepared solution containing 2 c.c. of $N/10$ iodine in 1 litre of water. The colours are to be compared in tubes 150 mm. long and 15 mm. wide, closed at the ends with glass plates and screw caps, having holes 12 mm. in diameter.

" *Reaction with Cadmium Chloride*.—10 c.c. of the pyridine bases are dissolved in 1 litre of water, and 10 c.c. of this solution are shaken with 5 c.c. of a solution of 5 grms. of anhydrous fused cadmium chloride in 100 c.c. of water. A copious separation of crystals should appear in ten minutes. The precipitate, collected on a filter of 9 cm. diameter, weighing 0·45 to 0·55 grm., drained and dried on filter-paper for one hour at 50° to 70° C. without washing, should weigh not less than 25 mgrms.

"*Reaction with Nessler's Reagent.*—10 c.c. of the same pyridine solution with 5 c.c. of Nessler's reagent should give a white precipitate.

"*Boiling-point.*—100 c.c. of the pyridine bases are measured into a short-necked flask of 180–200 c.c. capacity; the flask is placed on an asbestos plate with a circular hole, and a distillation head, with a bulb of the dimensions shown in fig. 52 is fitted and connected with a Liebig's condenser having a water column of at least 40 cm. length. At the other end an adaptor conducts the distillate into a narrow measuring cylinder of 100 c.c. capacity. The bulb of the thermometer must reach to the centre of the bulb in the head of the flask, and the column of mercury must be surrounded by the vapour. Distillation is conducted at the rate of 5 c.c. per minute. When the thermometer indicates 140° C. the flame is extinguished, and the volume of distillate is read when the liquid ceases to drop. The temperature is then raised to 160° C. and the same operation repeated. At least 50 c.c. should distil at temperatures up to 140° C., and 90 c.c. up to 160° C., the distillate being measured at 15° C.

"*Solubility in Water.*—50 c.c. of the sample of pyridine bases, when mixed with 100 c.c. of water, should give a clear or faintly opalescent mixture without separation of layers, which, after five minutes and before ten minutes have elapsed since mixing, should be sufficiently transparent in the 150 mm. tube to

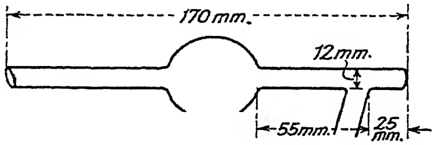


Fig. 52.—Boiling-point Apparatus.

allow printed characters to be read when the tube is held over them in a vertical position at such a distance that the printing is illuminated.

"*Moisture.*—20 c.c. of pyridine bases and 20 c.c. of caustic soda lye, sp. gr. 1·40, are measured by a pipette into a stoppered cylinder, graduated to $\frac{1}{5}$ c.c., and shaken. After settling, the upper layer should measure at least 18·5 c.c. at 15° C.

"*Titration.*—10 c.c. of pyridine bases are placed in a 100 c.c. flask containing 50 to 75 c.c. of water. The mixture is made up to the mark and shaken. 10 c.c. are then titrated with *N* sulphuric acid, using Congo paper as indicator, until a drop gives a distinctly blue edge, which then disappears. Not less than 9·5 c.c. of *N* acid should be required."

The Analysis of Mixtures Containing Organic Solvents.

The identification of a single solvent does not present much difficulty, but mixed solvents may be difficult or easy to separate according to the boiling-points of the individual constituents. Those met with in the textile industries are comparatively few in number, and as already noted are generally petroleum or aromatic hydrocarbons, pyridine, tetralin, hydrogenated phenols or chlorinated hydrocarbons. When a preparation containing soap or other similar constituents is being examined, the first thing to do is to separate the solvent. In some cases this can be done by ordinary distillation, the flask being immersed in a bath of melted paraffin wax and distillation continued until coloured

fumes make their appearance. When petroleum hydrocarbons with comparatively high boiling-points are present, it will be found convenient to distil off as much as possible directly and subject the residue to steam distillation. It must be noted that when *soaps* are present the mixture should either be made slightly acid before distilling with steam or sufficient calcium chloride or barium chloride added to decompose the soap. The range of boiling-points should be observed, but it is unnecessary to fractionate the distillate at this stage. Steam distillation may be employed from the beginning, but it must be remembered that water-soluble solvents such as pyridine will be dissolved. On the other hand steam distillation enables chlorinated hydrocarbons, which are heavier than water, to be detected at once. The distillate is measured or weighed. It is then dried, if necessary, by means of calcium chloride, sodium carbonate or sodium sulphate, and redistilled from a dry flask connected to a fractionating column. When steam distillation has been employed, the distillate is poured into a separating funnel and the aqueous layer drawn off. If the mixture was acidified before distillation the solvent layer should be washed with dilute sodium hydroxide solution to remove volatile fatty acids. It is then washed with water, dried and redistilled. The aqueous layer obtained from steam distillation is examined for alcohol, pyridine and acetone. When fractionating the dried distillate the temperatures of collection will depend upon the nature of the solvents present, and are varied accordingly.

CHAPTER XIV.

FORMALDEHYDE, TANNINS, "BLUEING" AGENTS, GLYCEROL.

Formaldehyde, HCHO.

FORMALDEHYDE is a gas which condenses at − 21° C. It is very soluble in water and a 30 to 40 per cent. aqueous solution of formaldehyde is known as *formalin.* When an aqueous solution of formaldehyde is allowed to stand, or is evaporated to dryness, an insoluble polymeride, *paraformaldehyde*, $(HCHO)_x$, is produced. When this substance is heated to a temperature of 140° C. another insoluble product, *trioxymethylene*, $(HCHO)_3$, is formed.

In order to detect formaldehyde in complex mixtures it must be removed by distillation either with water or steam. If present as a polymeride or condensation product, a little dilute sulphuric acid is added to the distilling flask.

Qualitative Tests.—In common with other aldehydes and ketones, formaldehyde gives a violet colour with *Schiff's reagent.* It forms *condensation compounds* with phenylhydrazine, hydroxylamine and semicarbazide, and unites directly with ammonia, sodium bisulphite and hydrocyanic acid. The most characteristic special tests are :

Hehner's Test.—A little of the solution containing formaldehyde is mixed with an equal volume of pure milk and the mixture is poured on to the surface of concentrated sulphuric acid to which a trace of ferric chloride has been added. A violet ring is formed after a few minutes at the junction of the two liquids. The presence of a protein and an oxidising agent are essential for the production of the colour. Lyons (*J.S.C.I.*, 1905, 1086) recommended the following modification as being capable of detecting one part of formaldehyde in 4,000,000 : Beef peptone is used instead of milk. To two test-tubes are added 2 c.c. of the solution under examination, containing 25 mgrms. of beef peptone, and the sulphuric acid to which a trace of ferric chloride has been added is poured carefully down the side of the tubes so as to form a layer at the bottom. One tube is allowed to stand until the colour zone develops. If the other is shaken to mix the contents a uniform violet colour is produced.

Phenol Test.—A drop of a dilute aqueous solution of phenol is added to the formaldehyde solution and the mixture is poured on to the surface of concentrated sulphuric acid in a test-tube. In the presence of formaldehyde a crimson ring is formed at the junction of the two liquids. Only a trace of phenol must be present.

Phenylhydrazine Test.—Formaldehyde gives a red colour with phenylhydrazine in the presence of a small quantity of a ferric salt. Arnold and Mentzel (*J.S.C.I.*, 1902, 725) described the following test : 5 c.c. of an alcoholic solution of formaldehyde are mixed with 0·03 grm. of phenylhydrazine hydrochloride and 4 drops of ferric chloride solution. 10 drops of concentrated sulphuric acid are then added, the mixture being kept cool. In Rimini's test, 2 drops of phenylhydrazine hydrochloride solution are added to the liquid under examination, then a drop of freshly prepared sodium nitroprusside solution

and a few drops of sodium hydroxide solution. In the presence of formaldehyde a deep blue colour is produced which changes through green and brown to red.

Schryver's Test is very delicate. The solution containing formaldehyde (10 c.c.) is added to 2 c.c. of a freshly made and filtered one per cent. solution of phenylhydrazine hydrochloride. To this mixture is added 1 c.c. of a fresh 5 per cent. solution of potassium ferricyanide, followed by 4 c.c. of concentrated hydrochloric acid. A brilliant Magenta-like colour develops, which reaches its full intensity in a few minutes and lasts for several hours.

Determination.—*Hexamethylenetetramine Method.*—A measured volume of the solution, *e.g.*, 5 c.c., is placed in a stoppered bottle and 50 c.c. of normal ammonium hydroxide solution are added. The bottle is closed and allowed to stand for some hours. The ammonia and formaldehyde react in accordance with the equation

$$6\,HCHO + 4\,NH_3 = (CH_2)_6N_4 + 6\,H_2O.$$

The unused ammonia is determined by titration with normal acid. The formaldehyde must be carefully neutralised before making the determination. The method is simple but not very accurate.

Romijn's Method is reliable. It depends upon the interaction of iodine with formaldehyde to give hydriodic and formic acids :

$$HCHO + I_2 + H_2O = 2\,HI + HCOOH.$$

A suitable volume of the formaldehyde solution (*e.g.*, 10 c.c.) is weighed in a stoppered weighing bottle, washed into a 500 c.c. flask and diluted to the mark with distilled water. 5 c.c. of this solution are transferred to a stoppered bottle and about 30 c.c. of normal sodium hydroxide solution added, followed by an excess of decinormal iodine solution, that is, sufficient to give the solution a distinctly yellow colour. The contents of the bottle are mixed well and if necessary more iodine solution is added. After about half an hour, decinormal sulphuric acid is added and the unused iodine determined by titration with sodium thiosulphate solution. Each cubic centimetre of decinormal iodine used up is equivalent to 0·0015 grm. of formaldehyde.

Another method due to Romijn depends upon the reaction

$$HCHO + KCN = CN\,.\,CH_2OK.$$

The formaldehyde solution is allowed to act upon a known excess of a standard solution of potassium cyanide, the unused portion being determined subsequently by titration with decinormal silver nitrate solution, potassium thiocyanate being used as indicator. Formaldehyde in combination with amino-acid residues is not affected by potassium cyanide, and thus only free formaldehyde is estimated.

Elvove (*Analyst*, 1911, 595) recommended the following procedure : About 0·5 grm. of the sample is weighed into a stoppered 150 c.c. Erlenmeyer flask and treated immediately with 100 c.c. of standardised potassium cyanide solution (about 6·5 grms. per litre). After thorough mixing, the contents of the flask are added to a mixture of 40 c.c. of decinormal silver nitrate solution and 10 c.c. of 10 per cent. nitric acid, the washings added, the whole made up to 200 c.c., shaken and filtered. The excess of silver nitrate in 100 c.c. of the filtrate is determined by titration with decinormal potassium thiocyanate solution, ferric ammonium sulphate being used as indicator. The amount of potassium cyanide in terms of decinormal silver nitrate solution which has

entered into combination with the formaldehyde multiplied by 0·3 and divided by the weight of the sample gives the percentage by weight of formaldehyde.

Finkenbeiner's Method (*J.S.C.I.*, 1899, 79).—In this method the formaldehyde is oxidised to formic acid by means of hydrogen peroxide in the presence of a known volume of standard sodium hydroxide solution. About 3 grms. of the neutralised formaldehyde solution are added to 50 c.c. of normal sodium hydroxide solution in a conical flask and 50 c.c. of pure neutral 3 per cent. hydrogen peroxide are added gradually by means of a tap funnel. The mixture is allowed to stand for an hour, after which the unneutralised alkali is determined by titration. The reaction is represented by the equations

$$H_2O_2 + HCHO = H_2O + HCOOH,$$
$$HCOOH + NaOH = HCOONa + H_2O.$$

Other methods include that of Lemme (*J.S.C.I.*, 1903, 1107), which depends upon the fact that when formaldehyde reacts with a neutral solution of sodium sulphite sodium hydroxide is formed in accordance with the equation

$$HCHO + Na_2SO_3 + H_2O = CH_2O \,.\, HNaSO_3 + NaOH.$$

In the method of Romeo (*Annali Chim. Appl.*, 1925, 300) potassium bisulphite is employed, the reaction being

$$KHSO_3 + HCHO = CH_2O \,.\, HSO_3K.$$

The excess of bisulphite is determined by titration with decinormal sodium hydroxide solution in the presence of phenolphthalein.

Colorimetric Method.—When only small quantities of formaldehyde are present a colorimetric method must be made use of. Schryver's method may be made quantitative by making up a series of standards with different quantities of formaldehyde. The reaction with sulphuric acid and ferric chloride in the presence of protein or peptone is capable also of giving quantitative results. The reaction with phloroglucinol is satisfactory for colorimetric determinations of formaldehyde. The reagent is made by dissolving 0·1 grm. of phloroglucinol in 10 c.c. of 10 per cent. sodium hydroxide solution. A known volume of the formaldehyde solution is placed in a Nessler cylinder, 2 c.c. of the reagent added and the volume of the mixture made up to 50 c.c. with distilled water. At the same time a number of standards are prepared containing varying quantities of formaldehyde. After three minutes the colours are compared.

The Analysis of Tannins.

The analysis of tannic acid or natural tans is complicated by the facts that the constitution of tannic acid is unknown and that the acid cannot be separated quantitatively as a precipitate of definite composition. Gallic acid, which is formed by the hydrolysis of tannic acid, but which has no value as a mordant, is also co-estimated with tannic acid by some of the methods of analysis employed. Many methods have been proposed; that selected will depend upon the purpose for which the tanning material is required. The tanner includes as tannic acid all that is absorbed by a purified chromed hide powder under standard conditions, and samples are always analysed by this process. The information which it gives would not necessarily be of value to the dyer, since hide takes up other constituents of the tannin solution, besides true tans, which give weight or

otherwise modify the nature of the leather produced. Hence the standard hide-powder method of analysis is rejected in favour of other methods, which are designed to give the information required. The methods of analysis available may be divided into the following groups:

(1) The Löwenthal method.
(2) Precipitation by means of metals.
(3) Precipitation with organic bases.
(4) Precipitation by means of basic dyestuffs.
(5) Dyeing tests.

The Löwenthal Method.—This is a volumetric process applicable to all kinds of tannins, and depends upon the fact that tannic acid is oxidised to a colourless compound by an acidified solution of potassium permanganate. It has, however, the disadvantage that gallic acid is simultaneously oxidised and hence returned as tannic acid. The following solutions are required:

1. *Standard potassium permanganate solution.*—A decinormal solution may be used, or a stock solution containing 5 grms. per litre, which is diluted to five times its volume for use.

2. A solution of 5 grms. of *indigo carmine* in one litre of 5 per cent. sulphuric acid.

3. *Gelatin solution*, which must be prepared freshly for each analysis. This is made by soaking 3 grms. of gelatin in cold water, dissolving the jelly and diluting the solution to 100 c.c.

4. A *saturated solution of sodium chloride* to which 50 grms. of sulphuric acid per litre have been added.

The permanganate solution is standardised against pure gallotannic acid. The stock solution is diluted to five times its volume with distilled water and a solution of the gallotannic acid containing about 3 grms. per litre is prepared. 10 c.c. of this solution are placed in a porcelain dish of at least 750 c.c. capacity and 20 c.c. of the indigo carmine solution and 750 c.c. of water are added. The permanganate solution is then run in from a burette until a faint pink colour appears, which is observed best around the side of the dish. Towards the end of the titration the permanganate must be run in drop by drop and time allowed after each addition for the reaction to be completed. A second titration is now made using 20 c.c. of indigo carmine solution and 750 c.c. of water. The difference between the two titrations gives the volume of permanganate solution required by 10 c.c. of the gallotannic acid solution. A quantity of the tannin is now weighed out, extracted with water, washed into a litre flask and diluted to the mark. The quantity of the tannin material weighed out should be such that the solution contains from 0·3 to 0·5 per cent. of tannic acid. The solution is filtered through a hard filter paper until it is perfectly clear. The filtrate is now titrated with the diluted permanganate solution, 10 c.c. of the tannin solution, 20 c.c. of indigo carmine solution and 750 c.c. of water being used as before. Since there may be other bodies present besides tannic acid capable of being oxidised by potassium permanganate, these are next determined in the following manner: 50 c.c. of the filtered liquor are pipetted into a 100 c.c. flask, mixed with 25 c.c. of the gelatin solution and diluted to 100 c.c. with the salt solution. A little kaolin is added and, after mixing well, the liquid is filtered. The gelatin will precipitate the whole of the tannic acid. Other compounds capable of being oxidised by permanganate will be in the filtrate. These are determined by titrating 20 c.c. of the filtrate (equal to 10 c.c. of the original solution) with the permanganate solution in the same manner as before. The

difference between the two readings gives the volume of permanganate required to oxidise the tannic acid present in 10 c.c. of the solution.

Precipitation by Means of Metals.—The tannates of the heavy metals and alkaline earth metals are generally insoluble in water, but the composition of the precipitate produced varies with the nature of the tannin material. A gravimetric method of determination due to Ruoss (*Analyst*, 1903, 118) depends upon the formation of a basic tannate of iron, $C_{10}H_9O_9 . FeO$, which, on drying at 100°–120° C. is changed into a compound having the composition represented by the formula $C_{14}H_7O_9Fe$, which, when ignited, gives iron oxide, Fe_2O_3. A simpler method is that of Richards and Palmer: A standard solution of potassium antimony tartrate (previously dried at 100° C.) is prepared containing 6·65 grms. per litre, each cubic centimetre of this solution being equivalent to 0·01 grm. of digallic acid. A measured volume of the tannin solution is placed in a dish or beaker, a little ammonium acetate added, and the antimony solution run in from a burette until the tannic acid is completely precipitated. The end-point of the reaction is detected by allowing the precipitate to settle, placing a drop of the supernatant liquid on a porcelain plate and adding a drop of sodium sulphide solution. As soon as an excess of the antimony solution is present the red colour of antimony sulphide will be observed.

Precipitation by Means of Organic Bases.—Tannic acid forms insoluble compounds with many organic bases, such as the basic dyestuffs and alkaloids, in the absence of mineral acids. The writer based a method of determination upon the formation of tannate of strychnine, but it has obvious disadvantages. Chapman used *cinchonine*, which has the advantage of being non-poisonous, although the tannate is not so suitable for separation. The method is simple: The solution of the tannin is treated with an excess of a solution of cinchonine sulphate, the precipitate filtered off on a weighed Gooch crucible, washed with a cold saturated aqueous solution of cinchonine sulphate, dried at 100° C. and weighed. The weight of the precipitate multiplied by 0·63 gives the tannic acid in the volume of the solution used.

Basic dyestuffs, such as Methylene Blue or Safranine, may be used as precipitants. In the method of Specht and Lorenz (*Analyst*, 1900, 163) the tannic acid is precipitated by Safranine in the presence of potassium antimony tartrate. About 0·16 grm. of the tannin, 0·2 grm. of potassium antimony tartrate and 0·33 grm. of pure Safranine are dissolved separately in water. The solutions are mixed, diluted to two litres with water, and the mixture allowed to stand for 6 hours, with occasional shaking. The precipitate is filtered off and the excess of Safranine is determined in a portion of the filtrate by running in a standard solution of sodium hydrosulphite until the colour disappears. The water used throughout must be boiled for some minutes to expel air, and cooled quickly. Parallel experiments are carried out with a solution of digallic acid. It is advisable to carry out the titration under a layer of petroleum or in the presence of an inert gas such as carbon dioxide.

In the method of Wilhelm (*J.S.C.I.*, 1898, 957), Methylene Blue solution is used, made by dissolving 12·5 grms. of the pure dyestuff in one litre of water. To 20 c.c. of this solution are added 10 c.c. of ammonia solution containing 100 grms. of 12·5 per cent. ammonia per litre. The solution of the tannin is then run in from a burette until all the Methylene Blue has been precipitated. This point is ascertained by placing a spot of the colour liquid on a filter paper, the end-point being the disappearance of the coloured halo which surrounds the spot when excess of the dyestuff is present. 1 grm. of Methylene Blue is equivalent to 0·49 grm. of digallic acid.

Dyeing Tests.—Actual dyeing tests, although purely empirical, have some

advantages. These may be carried out in the following manner: A solution of the tannin is made to contain the equivalent of about 0·3 grm. of tannic acid in 500 c.c. of water. This is heated to 90° C. and 10 grms. of scoured unbleached cotton are placed in the hot solution and left in it overnight. The cotton is then squeezed and soaked in a solution of ferric nitrate (sp. gr. 1·01–1·02) for one hour, after which it is squeezed and returned to the tannin solution for an hour, then rinsed and dried. The tanned cotton is now dyed with 20 per cent. *logwood extract* or 4–6 per cent. *hæmatin*, then treated for an hour with 0·5 per cent. potassium bichromate solution, washed, soaped and dried. The colour of the dyed sample is then estimated or compared with that produced using a standard sample of the tannin.

In a second method the cotton is mordanted with a solution of the tannic acid as before and then soaked in a 1 per cent. solution of tartar emetic, after which it is dyed in a solution of a basic dyestuff. Samples of cutch may be compared without subsequent dyeing; cotton is mordanted with a solution of the sample in the manner described above, then treated for three-quarters of an hour with a 0·5 per cent. solution of potassium bichromate, again tanned, washed and dried.

"Blueing" Agents.

Ultramarine.—This occurs in nature as *lapis lazuli*, a greenish-blue or violet-coloured mineral. It consists principally of the silicates of aluminium and sodium, together with sodium polysulphide. It is made by igniting a mixture of china clay, caustic soda or sodium carbonate, charcoal and sulphur, in the absence of air. A green substance is obtained which is heated again until the required tint is produced. Its approximate composition is

Silica,	40·88	per cent.
Alumina,	24·11	,,
Sulphur,	13·74	,,
Sodium oxide,	15·61	,,
Water,	5·66	,,

Ultramarine is insoluble in water and alkalis, but is decomposed by acids with evolution of sulphuretted hydrogen and a change of the blue colour to brown. It forms a reddish compound with chlorine. It is rarely adulterated, but different samples have not necessarily the same *colouring power*. This power depends upon the composition and fineness of the compound. It can be measured by mixing a weighed quantity of the substance with a white inert powder such as kaolin until the mixture has the same tint as one prepared from a standard sample. *Fineness* is measured by means of a sieve of definite mesh.

Smalt.—This is essentially glass, coloured with a little cobalt oxide, and it is made by fusing a mixture of silica, potash and oxide of cobalt, the depth of colour depending upon the proportion of cobalt present, commercial samples containing about 9 per cent.

Smalt is insoluble in water, acids and alkalis. It is adulterated sometimes with *ultramarine*. Its *colouring power* is tested in the same way as that of ultramarine. When ultramarine is present the colour is affected by dilute acids. Occasionally barytes or calcium sulphate coloured with a coal tar dyestuff may be substituted for smalt or ultramarine. In the latter case the colouring

matter could be extracted by means of water, alcohol or some other solvent. The colour of smalt is not changed by heating. When it has been used for the "blueing" of cotton or starch, minute blue specks can always be detected in the ash of the material; coal tar dyestuffs, on the other hand, are destroyed when the sample is ashed. Hence, if the colour of a smalt is destroyed or altered by igniting it in a silica dish, the sample must be adulterated.

Prussian Blue.—This is obtained as a blue precipitate by adding a solution of a ferric salt to one containing ferrocyanide. Its composition is represented by the formula $Fe_4[Fe(CN)_6]_3$. It is insoluble in hydrochloric acid but dissolves in oxalic acid, giving a deep blue solution, and it forms a violet solution in ammonium tartrate.

Detection.—Prussian blue may be identified by distilling it with dilute sulphuric acid and collecting the distillate in sodium hydroxide. Hydrocyanic acid distils over and combines with the sodium hydroxide to form sodium cyanide. A little ferrous sulphate and ferric chloride are added to the distillate and, after warming the mixture gently for a few minutes, it is acidified with hydrochloric acid, when Prussian blue is formed.

A fabric may be extracted with cold dilute sodium hydroxide or sodium carbonate and the washings filtered and tested in the same way.

Analysis.—The following method is due to Schmidt and Rassow (*Zeitsch. angew. Chem.*, 1924, **37**, 333): The finely ground material is treated with 2 *N* potassium hydroxide solution and the liquid filtered. Sodium hydroxide acts much more slowly and causes the ferric hydroxide to be precipitated in a very finely divided form, which is difficult to filter. The *ferrocyanide* in the filtrate is determined volumetrically by Mecklenburg's method, *i.e.*, by oxidation with permanganate in acetic acid solution and titration of the excess of permanganate with potassium iodide and thiosulphate. The precipitated ferric hydroxide is dissolved in hot dilute sulphuric acid, the solution reduced by allowing it to flow through a layer of amalgamated zinc, and titrated with permanganate. The *total iron* and any *potassium* are determined in another portion, the sample being heated to redness and dissolved in concentrated hydrochloric acid. The iron is determined by precipitating with ammonia and the potassium as sulphate in the filtrate. *Moisture* is usually determined by heating at 110° C., but more constant results are obtained by heating *in vacuo* at 90° C. The whole of the moisture can only be determined by heating the powdered substance, mixed with potassium bichromate, to bright redness and collecting the water given off in a calcium chloride tube. The *colour* of samples of Prussian blue is compared by mixing them to a paste with 20 parts of barium sulphate and painting them on to white cellulose paper. Purified Prussian blue, practically free from potassium, shows considerably less intensity of colour than good commercial samples. A typical analysis of a "Paris blue" was: Total iron 34·56 per cent., potassium 9·79 per cent., total water 10·13 per cent. (of which 5·92 per cent. was removed by heating *in vacuo* at 90° C.), cyanogen (by difference) 45·52 per cent.

Glycerol, $C_3H_5(OH)_3$.

Glycerol is obtained as a by-product in the preparation of soap by saponifying fats with caustic soda or by means of superheated steam or a hydrolysing agent such as Twitchell reagent or lipase. It is a transparent, colourless, odourless liquid, with a sweet taste. Its specific gravity is 1·265 at 15° C. It dissolves in water and alcohol but is insoluble in ether and chloroform.

Qualitative Reactions.—When glycerin is heated with concentrated sulphuric acid it chars and gives off *acroleïn*, which has an irritating odour. Acroleïn is produced also when potassium hydrogen sulphate is substituted for sulphuric acid, but very little charring occurs. Glycerol inhibits the precipitation of copper hydroxide by alkalis from solutions of copper salts: Loewe's reagent is founded upon this reaction. Unlike in the presence of sugar, no precipitate is produced even when the mixture is boiled. When a borax bead is soaked in a faintly alkaline solution of glycerol and heated in a Bunsen flame, a green colour is produced, owing to the liberation of boric acid. These tests are sufficient to identify glycerol when present in considerable quantities, but are not very delicate.

Schotten-Baumann Test.—When glycerol in aqueous solution is shaken with benzoyl chloride in the presence of caustic soda, a crystalline diglyceryl benzoate is formed which, after crystallisation from alcohol, has a melting-point of 72° C. to 73° C.

Déniges' Reaction.—This is based upon the fact that glycerol, when oxidised with bromine water, yields dihydroxyacetone, which gives characteristic colour reactions with phenolic compounds. Smith (*J.T.I.*, 1926, T 187) gives the following directions: 0·1 grm. of glycerol is heated on a water-bath with 10 c.c. of 0·3 per cent. bromine water for 20 minutes, or until the yellow colour due to bromine disappears. It then contains dihydroxyacetone, which gives the following colour reactions, the reagents being used in 5 per cent. alcoholic solution:

Volume of Solution.	Reagent.	Sulphuric Acid.	Method.	Result.
0·2 c.c.	0·1 c.c. codeine.	2 c.c.	Heat on water-bath for 2 mins.	Clear greenish-blue.
0·4 c.c.	0·1 c.c. β-naphthol.	2 c.c.	do.	Emerald green, with strong fluorescence.
0·4 c.c.	0·1 c.c. of 4 per cent. KBr, 0·1 c.c. salicylic acid.	2 c.c.	do.	Violet or wine red colour.
0·4 c.c.	0·1 c.c. thymol.	2 c.c.	Cold.	Pale rose to blood red.
0·4 c.c.	0·1 c.c. resorcinol.	2 c.c.	do.	Yellow to orange.

Another test depends upon the production of *α-naphthyl urethane*. A little of the extract is heated gently in a dry test-tube with five times its weight of α-naphthyl *iso*cyanate until a vigorous reaction sets in. The mass is then allowed to solidify and is recrystallised from pyridine. The melting-point of the urethane should be 278–280° C., but softening commences at 270° C. or lower.

Determination.—Commercial glycerin should not contain chlorides or sulphates, nor any compounds of metals. It should be free from fatty acids or other organic matter, and contain only traces of iron and lead. *Fatty acids* may be detected by the odour produced when the sample is mixed with dilute sulphuric acid and warmed. When *organic matter* is present a dark colour is produced when the sample is mixed with an equal volume of concentrated sulphuric acid, the mixture being kept cold. When only glycerol and *water* are present the percentage of the latter may be deduced from the specific

gravity of the solution. The following table by Gerlach gives the relationship between specific gravity and percentage of glycerol :

GLYCERIN TABLE.

Glycerol, Per cent.	Sp. Gr. 15° C./15° C.	Glycerol, Per cent.	Sp. Gr. 15° C./15° C.	Glycerol, Per cent.	Sp. Gr. 15° C./15° C.
100	1·2653	86	1·2292	72	1·1906
99	1·2628	85	1·2265	71	1·1878
98	1·2602	84	1·2238	70	1·1850
97	1·2577	83	1·2211	65	1·1711
96	1·2552	82	1·2184	60	1·1570
95	1·2526	81	1·2157	55	1·1430
94	1·2501	80	1·2130	50	1·1290
93	1·2476	79	1·2102	45	1·1155
92	1·2451	78	1·2074	40	1·1020
91	1·2425	77	1·2046	35	1·0885
90	1·2400	76	1·2018	30	1·0750
89	1·2373	75	1·1990	25	1·0620
88	1·2346	74	1·1962	20	1·0490
87	1·2319	73	1·1934	10	1·0245

Glycerol may be determined volumetrically by the acetin or the bichromate method. In the former a weighed quantity of the glycerol is converted into triacetin and the quantity of alkali required to saponify this triacetin is determined by titration :

$$C_3H_5(OOCCH_3)_3 + 3\,NaOH = 3\,CH_3COONa + C_3H_5(OH)_3.$$

In the bichromate method the glycerol is oxidised with an excess of a standard solution of potassium bichromate in the presence of sulphuric acid and the unused bichromate determined by back-titration.

The Acetin Method.—1·25 to 1·5 grms. of the sample are weighed in a small flask of about 120 c.c. capacity, 3 grms. of anhydrous sodium acetate and 7·5 c.c. of pure acetic anhydride are added, and the flask is connected to a vertical condenser either by means of a ground glass joint or (preferably) a rubber bung which has been subjected previously to the action of hot acetic anhydride vapour. (Anhydrous sodium acetate is made by fusing the crystalline salt in a silica dish, avoiding charring. When no more water is given off the mass is cooled, powdered, and kept in a stoppered bottle.) The contents of the flask are boiled gently for one hour, care being taken to prevent the sodium acetate from drying on the sides. After heating the flask for the hour, its contents are allowed to cool and 50 c.c. of carbon dioxide-free distilled water heated to 80° C. are poured in through the condenser, care being taken to prevent the bung from becoming loose. The flask is warmed to 80° C. until solution of the contents is effected. The solution is then cooled without detaching the flask from the condenser. The condenser is rinsed down with carbon dioxide-free distilled water, the flask detached from the condenser, the bung rinsed with water and the solution filtered through an acid-washed filter paper into a hard glass flask of about one litre capacity, the flask having been washed thoroughly with cold carbon dioxide-free distilled water. 2 c.c. of a neutralised 0·5 per cent. solution of phenolphthalein are added and then a normal solution of sodium hydroxide solution, free from carbonate, until a faint pinkish-yellow colour is produced. The alkali is added towards the end very carefully, drop

by drop, since exact neutralisation is necessary. The sides of the flask are now rinsed down, 50 c.c. of normal sodium hydroxide solution are added, and the liquid boiled gently for 15 minutes to saponify the triacetin, a long air condenser being attached to the flask. The contents of the flask are cooled and the excess of sodium hydroxide determined by titration with normal hydrochloric or sulphuric acid, the end-point being the production of the pinkish-yellow colour already noted. A further addition of phenolphthalein at this point will cause the pink colour to return, but this must be neglected and the first end-point taken. Each cubic centimetre of normal alkali which has disappeared corresponds to 0·03069 grm. of glycerol. A blank test should be made with the acetic anhydride and sodium acetate. (International Standard Method, 1911).

The Bichromate Method (*ibid*).—The following solutions are required:

(*a*) Potassium bichromate solution, made by dissolving 7·4564 grms. of the pure salt in 1 litre of water.

(*b*) Ferrous ammonium sulphate solution, the value of which is known in terms of potassium bichromate.

(*c*) Silver carbonate, prepared for each test by treating 140 c.c. of 0·5 per cent. silver sulphate solution with about 4·9 c.c. of normal sodium carbonate solution, allowing the precipitate to settle, decanting and washing once by decantation. It should be noted that excess of sodium carbonate prevents rapid settling of the precipitate.

(*d*) Subacetate of lead. A 10 per cent. solution of lead acetate is boiled for an hour with excess of litharge, keeping the volume of the liquid constant. The mixture is filtered whilst hot and any precipitate which forms subsequently is disregarded. The solution is kept out of contact with carbon dioxide.

(*e*) Potassium ferricyanide solution of 0·1 per cent. strength.

When making an analysis, 20 grms. of the glycerol are weighed out, dissolved in water and the solution diluted to 250 c.c., 25 c.c. being taken for the analysis. To this is added the silver carbonate prepared as described above, and the mixture allowed to stand for ten minutes, with occasional stirring. A slight excess (about 5 c.c.) of the lead acetate solution is then added and after a few minutes the mixture is diluted to 100 c.c. with distilled water and an extra 0·15 c.c. added to compensate for the volume of the precipitate. The mixture is now shaken and filtered through an air-dry filter into a narrow-mouthed vessel, the first 10 c.c. being rejected and the remainder returned to the filter if not clear and bright. A portion of the filtrate is tested with the lead acetate. No more precipitate should be formed. If a precipitate is produced a fresh determination must be started, using 6 c.c. of the lead acetate solution, but a marked excess must be avoided. A beaker is cleaned with potassium bichromate and sulphuric acid and 25 c.c. of the clear filtrate are pipetted in, 12 drops of sulphuric acid (1 : 4) being added to precipitate the lead. Next 3·7282 grms. of powdered potassium bichromate are introduced and rinsed down with 25 c.c. of water. After all the bichromate has dissolved (assisted by occasional shaking), 50 c.c. of 50 per cent. sulphuric acid are added and the flask is immersed in boiling water for two hours, being protected against entrance of dust or organic vapours such as alcohol until the titration is completed. A slight excess of the ferrous ammonium sulphate solution is now added from a weighing bottle, making spot tests with the potassium ferricyanide solution. The excess is then titrated back with the solution of potassium bichromate.

$$1 \text{ grm. of glycerol} \equiv 7{\cdot}4564 \text{ grms. bichromate.}$$
$$1 \text{ grm. bichromate} \equiv 0{\cdot}13411 \text{ grm. glycerol.}$$

This method was elaborated by a British Experts Committee and the details should be adhered to strictly.

Chapman (*Analyst*, 1926, 382) determines glycerol by converting it into *isopropyl iodide*, $CH_3 . CHI . CH_3$, which is passed into an alcoholic solution of silver nitrate, the precipitated silver iodide being filtered off and weighed. The method is very delicate, but requires special apparatus.

The Determination of Glycerol in Fabrics and Size.—The following method was described by Smith (*J. Text. Inst.*, 1926, T 187): The cloth is extracted for three hours in a Soxhlet extractor with 95 per cent. alcohol. The alcoholic solution is cooled, filtered and evaporated to about 2 c.c. on a water-bath. This residue is shaken with 20 c.c. of warm, very dilute hydrochloric acid, cooled and filtered, or extracted with ether to remove fatty matter. It is then boiled with a slight excess of sodium carbonate to remove zinc. When all the liberated carbon dioxide has been expelled a few drops of 10 per cent. sodium hydroxide solution are added to complete the precipitation of magnesium. The mixture is then filtered, neutralised carefully with hydrochloric acid and evaporated to about 5 c.c. If zinc and magnesium are known to be absent, the solution, after removing fatty matter, may be neutralised and evaporated at once. The residue is shaken with 1 c.c. of benzoyl chloride and 5 c.c. of 10 per cent. sodium hydroxide solution, together with 1 drop of methyl red. As soon as the precipitated glyceryl benzoate turns red, more alkali is added, a few drops at a time, with vigorous shaking, until the odour of benzoyl chloride disappears. The oily product is filtered off, washed with water and then dissolved without drying by pouring 2 c.c. of boiling alcohol on to the filter, which should be very small. The alcoholic solution is allowed to crystallise slowly in a small test-tube. At first some oily substance separates, and if crystallisation proceeds slowly, this all separates first and the glyceryl benzoate crystallises above it in clusters of fine needles. These crystals are separated and weighed and their melting-point determined (72°–73° C.).

Neale's Method (*J. Text. Inst.*, 1926, T 511).—In this method the glycerol is determined by moist combustion with potassium bichromate and sulphuric acid, measuring the carbon dioxide produced. In the case of yarn or cloth, 10 grms. of the sample are extracted in a hot Soxhlet apparatus with acetone for 4 hours. The extract is evaporated to dryness in the distilling flask, the residue extracted three times with 25 c.c. of a mixture of alcohol (2 vols.) and ether (1 vol.) and the solution filtered. For size, 2 grms. are ground with 40 c.c. of absolute alcohol, which is added little by little, after which 20 c.c. of ether are added and the clear liquid decanted. The extraction is repeated and the residue finally washed on a filter with alcohol-ether mixture. The extracts are now evaporated, the addition of a little boric acid reducing loss of glycerol. The last traces of alcohol are removed by passing a current of air through the flask on the steam bath. The residue is washed from the flask with 20 c.c. of dilute sulphuric acid (2 vols. water : 1 vol. acid) and shaken in a separating funnel with 60 c.c. of petroleum ether to remove fat. The aqueous layer is heated to remove petrol and then filtered into a gas burette over mercury. The burette is illustrated in fig. 53. After introducing the glycerin solution, 2 c.c. of 40 per cent. potassium bichromate are run in and the mixture is heated to 100° C. by means of the steam jacket. The gas evolved is collected in the second burette over mercury, the connection between the two burettes consisting of capillary tubing. The last traces of carbon dioxide are removed from the reaction burette by causing its contents to boil under reduced pressure, after the reaction has proceeded for an hour. The volume of the carbon dioxide, saturated with water vapour, is measured, and the small quantity of air (about

0·2 c.c.) determined by absorbing the carbon dioxide with caustic potash. The volume of the carbon dioxide is calculated to N.T.P. and the quantity of glycerol calculated from the factor

1 litre of dry carbon dioxide at N.T.P. ≡ 1·369 grms. glycerol.

The Determination of Glycerol in Fats, Oils, and Soaps.—A fat or oil is first saponified with alcoholic potash and the alcohol evaporated off on a water-bath. The residual soap is dissolved in water, the solution acidified with hydrochloric acid and the mixture heated on a water-bath until the fatty acids form a clear layer on the surface of the liquid. They are then filtered through a ribbed

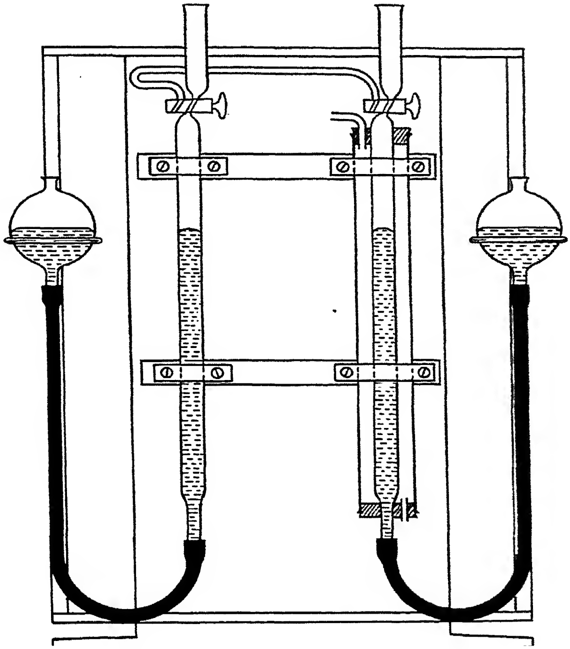


Fig. 53.—Neale's Burette.

filter paper, previously wetted with hot water, and washed with hot water until free from acid. The filtrate, which contains the glycerol, is neutralised with sodium hydroxide solution and some lead acetate solution is added. The precipitate formed is filtered off and washed. The filtrate is concentrated until crystals appear. These are removed with a small spoon, placed on a Gooch filter and sucked dry, the liquor being concentrated further. Finally, when about 5 c.c. remain, the crystals are added and the glycerol is extracted with a mixture of 3 volumes of spirit and one volume of ether. After evaporating off the solvent, the glycerol is determined by the acetin method. It is simpler to use barium carbonate instead of lead acetate and evaporate to dryness on the water-bath, extracting the residue with alcohol and ether.

CHAPTER XV.

STARCH, DEXTRIN, GLUE, GELATIN, CASEIN, AND VEGETABLE GUMS.

Starch.

The principal starches used for textile purposes are from potatoes (farina), maize (corn starch) and wheat. Tapioca starch and sago starch are used in sizing yarns and rice starch for laundry work. The origin of a starch is determined by microscopic examination. The appearance of the different granules is shown in fig. 54.

The following table gives some details of granule measurements :

Name. of Starch.	Outline of Granule.	Measurement.	Surface.	Hilum.	Markings.
Potato.	Oval.	mm. 1/25 long diam. 1/37 short ,,	Uniform and slightly convex.	Dark spot near the narrow end.	Concentric rings, closed or almost closed curves.
Rice.	Rectilinear and polygonal.	1/250 diam.	Flat.	None.	None.
Maize.	Rectilinear and polygonal.	1/70 diam.	Uneven and slightly concave.	Stellate or irregular large central hilum.	None.
Wheat.	Circular or nearly so.	1/50 diam.	Convex.	Dark spot, eccentric.	Occasionally a few exceedingly faint concentric rings.
Arrowroot (Bermuda).	Oval.	1/28 long diam. 1/45 short ,,	Uniform and slightly convex.	Nearer broad end, circular crucial transverse line or slit.	Faint concentric rings, in a few cases extending about ⅔ length of grain.
Cassava.	Rectilinear and polygonal.	1/70 diam.	Uneven and slightly concave.	Stellate or irregular large central hilum.	None.

There is no chemical method for determining the proportions of the constituents of a mixture of starches, but an approximate analysis may be made by the following process : Mixtures are made of the starches known to be present and containing varying proportions of each. These are compared with the original sample until a mixture is found which has approximately the same composition as the sample.

If microscopic examination of a sample of potato starch showed that it contained a small proportion of maize starch, mixtures containing 5, 10, 15, 20 and 30 per cent. of the latter would be made by grinding weighed quantities of each in a mortar. 0·1 grm. of the original sample is weighed out and ground with a little water in an agate mortar, the mixture washed into a small graduated cylinder and made up to 10 c.c. with water. One drop of the mixture is placed on a slide and covered with a coverslip. The slide is then examined and the

number of maize granules is counted in ten different fields. The standard mixtures are examined also in the same manner, until one is found which gives the same number of maize granules per field as the sample. The microscopic examination of starch is assisted by lightly staining with a basic dyestuff such as Methylene Blue.

The Analysis of Starch.—Both physical and chemical tests are employed in the analysis of starch. The former are for many purposes the more important, and will be described first.

Physical Tests.—*Gelatinising Temperature.*—This is determined by mixing a little of the starch with cold water in a test-tube and heating the tube in a water-bath, stirring the mixture with a thermometer until incipient thickening,

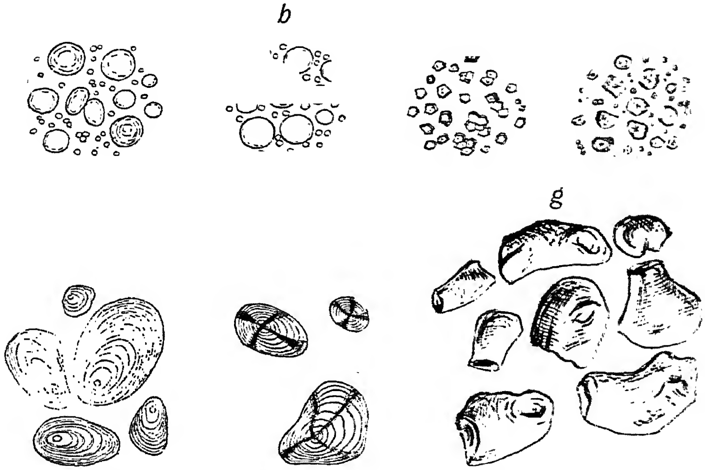


Fig. 54.—Starch Granules from—(*a*) barley; (*b*) wheat; (*c*) rice; (*d*) maize; (*e*) potato; (*f*) potato, in polarised light, × 300 (*Stirling*); (*g*) sago (*Davies*).

indicating gelatinisation, is observed, when the temperature is noted. The gelatinising temperatures of the common starches are:

Potato starch,	65° C.
Wheat starch,	70° C.
Maize starch,	70° C.
Sago starch,	72° C.
Tapioca starch,	75° C.

Viscosity.—The viscosity of a starch solution varies with the nature of the starch but is approximately constant for the same concentration of the same starch. McNider (*J. Ind. Eng. Chem.*, 1912, 417) gives the following figures for solutions containing 12 grms. of starch in 30 c.c. of water:

Potato starch,	14·3
Maize starch,	2·5
Wheat starch,	1·2
Rice starch,	1·0

It is very difficult to determine the viscosity of a starch solution with a pipette form of viscometer, since the orifice is liable to become clogged. Some form of falling sphere apparatus should be used. That described by Gibson and Jacobs (*J.S.C.I.*, 1920, 558 A) is simple to construct: A glass tube, 29 cm. in length and having an internal diameter of 2 cm., is clamped vertically in a bath provided with a stirrer and thermometer. The tube is divided into three 5 cm.-lengths for measurement of the time of fall of the ball, with a further 5 cm. marked at the top to allow the ball to acquire uniform velocity before measurements are taken. A steel ball (0·15 cm. in diameter) is used, such as is employed for ball bearings. It is introduced into the tube by means of a short length of glass tubing, 3 mm. in diameter, fixed by means of a rubber bung and adjusted to dip 3 cm. below the surface of the liquid. The time of fall is observed with a stop watch. The viscosity is given by the equation

$$\eta = K (s - \sigma) T,$$

where K is a constant involving all the corrections for the tube, s is the density of the sphere and σ that of the liquid. The constant K is found by experiment with a liquid of known viscosity.

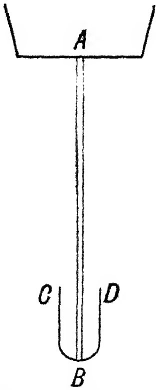


Fig. 55.—Apparatus for Determination of Breaking Strength of Starch Jelly.

Ermen's Method (*The Materials Used in Sizing*, p. 8) is a good one. It depends upon the fact that different starches give different but constant viscosities when dissolved in a solution of sodium hydroxide. 3·5 grms. of the starch are washed into a 250 c.c. flask with 230 c.c. of distilled water, 15 c.c. of standardised 10 per cent. sodium hydroxide solution added, and the contents of the flask shaken and made up to 250 c.c. with cold water. The flask is then shaken until the starch has dissolved completely. It is then allowed to stand for twelve hours, after which the viscosity of the solution is determined.

Stiffening Power.—5 grms. of the starch are made into a cream with 20 c.c. of water and poured with constant stirring into 100 c.c. of boiling water, the mixture afterwards being heated in a water-bath until the whole is gelatinised. The paste is then allowed to cool and the weight which it will bear is measured. The apparatus illustrated in fig. 55 is suitable for the purpose. The small cup CBD is placed on the surface of the paste. The apparatus is supported in a vertical position by means of a bored cork. Shot is then poured carefully into the upper cup A until the lower cup breaks the surface of the paste. The weight of the apparatus and shot are a measure of the strength of the paste. Suitable dimensions are CD = $\frac{1}{2}$ inch, AB = 9 inches. This test gives rather variable results, since the strength of the paste formed is determined by the proportion of granules which are completely gelatinised.

Harrison (*J. Soc. Dyers and Col.*, 1911, 84) described the following method: 1 grm. of the sample is suspended in 100 c.c. of cold water and heated with stirring to a temperature slightly above its gelatinising point. The mixture is then cooled and centrifuged in a tube graduated in tenths of a centimetre. The ungelatinised granules are thus separated, and their volume is inversely proportional to the stiffening power of the starch.

Chemical Analysis.—A general analysis includes the determination of

(*a*) *moisture*, (*b*) *ash*, (*c*) *matters soluble in cold water*, (*d*) *starch* by difference or by direct determination.

The *soluble matter* may consist of dextrin, dextrose, soluble starch or salts. *Acidity* or *alkalinity* should be determined in the aqueous extract, since alkaline starches thicken on boiling, whilst acid starches become thin. *Sulphurous acid*, if present, is determined by distilling with steam into hydrogen peroxide and weighing the sulphuric acid produced as barium sulphate.

It is of importance to note whether the soluble matter obtained by evaporating the aqueous extract becomes brown when dried. This is often the case with thin starches, and is sometimes the cause of discoloration in cotton goods.

Blueing agents should be looked for, since they are added sometimes to low-grade starches to improve the colour. Smalt can be recognised as blue particles in the ash. Starches containing ultramarine become discoloured when moistened with acids, whilst coal tar dyestuffs can be extracted with water or alcohol and dyed on wool.

Determination.—The difference between 100 per cent. and the sum of the moisture, ash and soluble matter may be regarded as *starch*. This includes any cellulose which may be present, but the error introduced is very small.

Starch may be determined quantitatively by boiling a weighed quantity of the sample with dilute hydrochloric acid and determining the *dextrose* formed by means of *Fehling's solution*, 10 parts of starch giving 9 parts of dextrose after inversion. The method is, however, not very accurate, since it is difficult to convert the whole of the dextrin into dextrose without producing secondary products of decomposition. The sample should be extracted with 70 per cent. alcohol to remove sugars before making the analysis. The factor for converting cupric oxide into starch is 0·4081.

Starch may be *inverted* by means of *diastase* or *Taka diastase*, a mixture of dextrose and maltose being produced. In the method of Davis (*J.S.C.I.*, 1916, 207), 2 grms. of the sample, after extraction with alcohol, are heated with 200 c.c. of water until completely gelatinised. The mixture is cooled to 38° C., 0·1 grm. of Taka diastase and 2 c.c. of toluene added, and the mixture digested for 24 hours at 38° C. It is then heated to 100° C., filtered into a 500 c.c. flask and the filter washed until the filtrate measures 475 c.c. Lead acetate solution is then added, the mixture cooled, made up to 500 c.c. and filtered. The lead is precipitated in 100 c.c. of the filtrate by adding sodium carbonate, after which the volume is made up to 110 c.c. and the mixture filtered. The *rotation* and *reducing power* of the filtrate are determined and the original starch calculated from the results.

Von Fellenberg (*J.S.C.I.*, 1917, 935) based a method for the determination of starch upon its *solubility in* a solution of *calcium chloride*: 0·3–1 grm. of the finely ground fat-free material is moistened with water and mixed with 20 c.c. of 50 per cent. calcium chloride solution. The mixture is then heated in boiling water for 30 minutes to dissolve the starch. It is then cooled, made up to 100 c.c. and filtered or centrifuged. 50 c.c. of the resulting liquid are treated with $N/50$ iodine solution until a flocculent precipitate is obtained, but avoiding a large excess of the reagent. After standing for 24 hours a little asbestos pulp is added and the mixture filtered through an asbestos mat in a Gooch crucible. The precipitate is washed four times with 5 per cent. calcium chloride solution containing a little iodine, and then with 60, 85 and 95 per cent. alcohol successively. The crucible is then dried and weighed. It is then ignited and weighed again. The difference between the two weights gives the amount of starch present.

When mixed with bodies which are insoluble in alkalis, starch can be estimated with approximate accuracy by treating the sample with cold dilute *sodium hydroxide* solution to dissolve out the starch and then precipitating with excess of *alcohol*.

The most accurate method of determining starch is by means of the *polarimeter*. In Lintner's method (*J.S.C.I.*, 1907, 281), 5 grms. of the starch are ground to a smooth paste with 20 c.c. of water. 40 c.c. of hydrochloric acid (sp. gr. 1·19) are then added and the mixture allowed to stand for 30 minutes to dissolve the starch. The liquid is then washed into a 200 c.c. flask with hydrochloric acid of 1·125 sp. gr. Proteins, if present, are precipitated by adding 10 c.c. of a 4 per cent. solution of phosphotungstic acid. The mixture is made up to 200 c.c. with the dilute hydrochloric acid, shaken and filtered. The rotation of the filtrate is measured in a 200 mm. tube. If soluble carbohydrates are present a control experiment is necessary. For this, 5 grms. of the starch are digested with 70 c.c. of water at 50° C. for an hour. 25 c.c. of glacial acetic acid are then added and the digestion continued as before, the mixture then being made up to 100 c.c., filtered and its rotation measured. The starch content is calculated from the following values for α (specific rotatory power for sodium light):

Wheat starch,	+182·62
Rice starch,	+183·62
Maize starch,	+184·19
Potato starch,	+186·46.

Thorne and Jeffers' modification of Lintner's process (*Analyst*, 1909, 332) is recommended by Baker, and the method is described in the *Reports to the Local Government Board on Public Health and Medical Subjects, New Series, No.* 80. For the estimation, 5 grms. of the substance are ground in a mortar with 10–15 c.c. of water, followed by 40 c.c. of hydrochloric acid (sp. gr. 1·15) added in quantities of 5 c.c. at a time. The starch quickly becomes a viscous mass, and this in the course of a few minutes becomes thin. After standing for half an hour the mixture is transferred to a 200 c.c. flask containing 10 c.c. of a 4 per cent. solution of phosphotungstic acid and 20 c.c. of hydrochloric acid of sp. gr. 1·15. The mortar is washed out with hydrochloric acid of 1·1 sp. gr. and the contents of the flask made up to the mark with acid of the same strength. After being well shaken and again allowed to stand for at least half an hour the liquid is filtered and its rotation measured in a 200 mm. tube at 20°.C. With a Schmidt and Haensch scale and white light the percentage of starch (P) is calculated from the rotation (R) by the formula

$$P = \frac{R \times 40}{11{\cdot}6}.$$

This formula involves the assumption that soluble starch has a specific rotatory power of + 200, a value probably somewhat too high.

Determination of Starch in Sized and Finished Cotton Goods (Fargher and Lecomber, *J.Text.Inst.*, 1931, T 475).—The method consists of hydrolysing the starch by means of sulphuric acid and determining by titration with iodine solution the glucose produced. A sample of the fabric weighing about 10 grms. is cut into small pieces (⅜ in. × ⅜ in.), these pieces mixed thoroughly, and the moisture content determined on a 1 grm. portion. At the same time 2·5 grms. are weighed, placed in a 100 c.c. conical flask and wetted-out by heating with water just to the boiling-point, the neck of the flask being closed with a com-

bined glass pear bulb and stirring rod. After cooling, 20 c.c. of 4 N sulphuric acid are added and the flask placed in a rapidly boiling water bath for $2\frac{1}{2}$ hours, the contents being stirred vigorously for the first three minutes. The flask is cooled again, the mixture filtered through a Buchner funnel and the cotton washed repeatedly with water, using 100 c.c. in all. 19 c.c. of 4 N sodium hydroxide solution are added slowly from a pipette to the filtrate, with vigorous stirring, and the solution diluted to 250 c.c. with water. Glucose is determined in this solution as follows: 25 c.c. of the solution are titrated with $N/2$ sodium hydroxide. The glucose is then determined in 50 c.c. of the solution by adding 25 c.c. of $N/20$ iodine solution, followed by the volume of $N/2$ sodium hydroxide solution required for neutralisation (as determined on the 25 c.c. portion) plus 3·12 c.c. The sodium hydroxide must be added slowly, and with constant shaking. After standing for 10 minutes at 20° C., the solution is acidified by adding 1·6 c.c. of 4 N sulphuric acid, and the excess of iodine is titrated with $N/20$ sodium thiosulphate solution. It is convenient to carry out the determination in a 250 c.c. glass-stoppered bottle. If more than three-fifths of the iodine are used up by the glucose, the titration must be repeated using 25 c.c. of the sample solution, whilst if the volume of iodine used is very small, 100 c.c. of the solution should be used. The result is calculated as follows:

If T c.c. of $N/20$ iodine are used up by 1 grm. of the sized sample, containing x per cent. of moisture, then 1 grm. of the dry sample will require $\frac{100\,\mathrm{T}}{100-x} = \mathrm{T}'$ c.c. Similarly if t c.c. of $N/20$ iodine are required by 1 grm. of the blank, containing y per cent. of moisture, then 1 grm. of the dry blank will require $\frac{100\,t}{100-y} = t'$ c.c. $= 8{\cdot}15$ c.c. if the mean correction for grey cotton is used, or 4·31 c.c. using the corresponding value for scoured cotton.

Then S, the starch content per cent., is given by

$$\mathrm{S} = 0{\cdot}417\left[\mathrm{T}' - t'\,\frac{(100-\mathrm{C})}{100}\right]$$

where C is the total size per cent., and 1 c.c. of $N/20$ iodine is equivalent to 0·00405 grm. pure starch or 0·00417 grm. of average commercial starch.

The blank determination is necessary to allow for substances other than starch which are present in cotton and react with iodine after hydrolysis. Experiments made with a large number of cottons showed that these bodies correspond to 3·0 to 4·9 per cent. of starch in the final result. Any gums which may be present, such as gum tragacanth or gum tragasol, are estimated substantially as starch, whilst Irish moss interferes to a less extent.

Total Size may be determined by the method of Clibbens and Geake (*J.Text.Inst.*, 1931, T 472). In this the sample is extracted for one hour with chloroform, dried by exposure to air, and washed by alternate immersion in hot running water and wringing by hand twelve times. The cotton is then alternately immersed in 0·5 per cent. diastafor solution (20 to 30 times the weight of cotton) at 50° C. and wrung by hand three times in succession, finally being returned to the solution which is then heated to 70° C. The cloth is allowed to remain in the solution 15 minutes in all. It is then washed in hot running water as before, dried at 110° C. side by side with a sample taken for moisture determination, and both are weighed. The size content of the material is calculated from its loss of weight on desizing, its moisture content and the

esizing blank, for which the mean value of 3 per cent. is adopted in the bsence of unsized controls.

Dextrin.

Dextrin has a variable composition depending upon the method of manuacture and the pure substance is never met with in commerce. The principal varieties are (1) *thin starch*, (2) *white dextrin*, (3) *canary dextrin*, (4) *yellow dextrin*. These differ in the proportions of starch, soluble starch, dextrin and dextrose which they contain. Acids and bleaching agents may be present as impurities.

Pure dextrin is a colourless substance without taste or smell. It has a specific rotation of about 200. It is readily soluble in water but is insoluble in organic solvents. When boiled with dilute hydrochloric or sulphuric acid it is changed into dextrose. Hot nitric acid of 1·35 sp. gr. converts it into oxalic acid, whereas vegetable gums yield mucic acid. Dextrin cannot be changed into alcohol by the action of yeast. It is precipitated from its solutions by an ammoniacal solution of lead acetate but not, like starch, by barium hydroxide. Dextrin may be recognised by the reddish-brown colour which it gives with iodine; but some types (*achrodextrins*) do not give this reaction.

Analysis.—The general analysis of dextrin is carried out in a similar manner to that of starch.

Moisture and Ash.—These are determined in the usual manner.

Soluble Matter.—About 5 grms. of the sample are weighed out, ground with a little cold water, washed into a 250 c.c. flask and the mixture diluted to the mark with cold water. The flask is then closed and allowed to stand for three or four hours, with occasional shaking. If any *insoluble residue* remains, the mixture is filtered through a weighed Gooch crucible. The residue is washed with cold water, then with alcohol, dried at a low temperature and weighed. After weighing, the crucible is ignited and weighed again. The second weight gives any *insoluble mineral matter* present. The difference between the first and second weights gives the *insoluble starch*. The dextrin in the filtrate may be determined by concentrating a measured portion to a syrup on the water-bath and adding about 10 volumes of 90 per cent. alcohol. The precipitate is filtered off, washed with 90 per cent. alcohol, dried and weighed.

In order to determine *gum*, about 1 grm. of the foregoing precipitate is dissolved in 16 c.c. of water, and 30 c.c. of proof spirit, 4 drops of a 20 per cent. solution of ferric chloride and a little powdered calcium carbonate are added. After stirring and allowing the mixture to stand for a short time, any precipitated gum is filtered off and washed with proof spirit. The *dextrin* is then precipitated in the filtrate by adding excess of 95 per cent. alcohol, filtered off, washed with alcohol, dried and weighed. *Dextrose* is determined in another portion of the aqueous solution by means of Fehling's solution.

The method of Babington, Tingle and Watson (*J.S.C.I.*, 1918, 257 T) is very useful. The following determinations are made: (*a*) Ash, (*b*) moisture, (*c*) dextrin gum, (*d*) insoluble starch, (*e*) reducing sugars, (*f*) total starch [$100 - (a + b + c)$], (*g*) soluble starch ($f - d$), (*h*) non-reducing dextrin gum ($c - e$). The *dextrin gum* is determined in the following manner: 1 grm. of the sample is warmed with 30 c.c. of water in a 100 c.c. flask until it just gelatinises; the mixture is then cooled quickly and 50 c.c. of a saturated solution of barium hydroxide are added. The contents of the flask are diluted to 100 c.c. with water, mixed and filtered. 50 c.c. of the filtrate are placed in a platinum or silica dish, a drop of phenolphthalein solution added and normal

hydrochloric acid run in until the mixture is just acid. The pink colour is then restored by careful addition of barium hydroxide solution, a weighed quantity of dry washed sand added and the contents of the dish evaporated to dryness on the water-bath. The dish is then dried at 120° C. to dehydrate the barium chloride and weighed. The organic matter is removed by incineration and the dish again weighed. The difference between the two weights gives the dextrin gum.

In the absence of other optically active bodies, *dextrin* may be determined directly by means of a polarimeter. 10 grms. of the sample are dissolved in about 50 c.c. of cold water and the solution treated with 5 c.c. of alumina cream. The mixture is diluted to 100 c.c., well mixed and filtered. The filtrate is examined in a 200 mm. tube and the specific rotation is calculated from the formula

$$\alpha_D = \frac{\alpha \times 100}{l\,c}$$

where α is the angle of rotation, l the length of the tube and c the concentration of the solution. The dextrin present is calculated from the specific rotation $\alpha_D = +200$.

Practically all commercial dextrins contain *dextrose*. This can be determined by means of Fehling's solution. Its specific rotatory power (α_D) is $+52{\cdot}7$. The rotation produced by the amount of dextrose found can be calculated and allowed for. Only cold water must be used in making up the solution, since if starch be dissolved it also will produce a rotation.

Dextrin and dextrose may be determined by means of Fehling's solution. A 10 per cent. cold water solution is made up and filtered. The *dextrose* is determined in a portion of the filtrate by heating with Fehling's solution in the manner described in Chapter IV. For this purpose 10 c.c. of the solution are diluted to 100 c.c. with water and 10 c.c. at this dilution are used. A second 10 c.c. are diluted to 50 c.c. with water containing 1·5 c.c. of concentrated sulphuric acid, heated on a water-bath for three hours, then cooled, made slightly alkaline and diluted to 100 c.c. The reducing power of this solution is now determined with Fehling's solution, that due to the dextrose is deducted and the remainder calculated to *dextrin.*

Glue and Gelatin.

Glue and gelatin are both prepared from the same raw material, namely bone or skin, the difference between them sometimes being apparent rather than real. Bones contain a nitrogenous substance termed ossein and skin a similar body known as collagen, both of which are hydrolysed when heated with water, with the formation of glutin or gelatin. This is hydrolysed further by prolonged heating with water, or rapidly when either acid or alkali is present, with the formation of soluble gelatoses, peptones and finally amino-acids. Glutin is the jelly-forming constituent of both glue and gelatin; gelatoses have adhesive power but do not form jellies; peptones and other nitrogenous degradation products are not only useless, but actually harmful, since they detract from the strength of the jelly, forming a hygroscopic film when dried, and also favouring the growth of putrefactive and other organisms. The lighter colour of gelatin is obtained by bleaching the liquors before setting and drying; it is partly due also to the fact that gelatin is cast into thinner cakes than glue. That appearance

s no criterion of quality is seen from the following examples of the composition of good and bad samples :

	Good Gelatin.	Poor Gelatin.	Good Glue.	Poor Glue.
	Per cent.	Per cent.	Per cent.	Per cent.
Water,	14·00	14·00	14·23	16·25
Mineral matter,	1·58	1·75	1·33	2·75
Gelatin,	80·00	75·00	78·08	64·35
Peptones and other nitrogenous bodies,	0·50	4·50	1·95	11·10
Non-gelatinous bodies,	3·92	4·75	4·41	5·55

The poor gelatin had a much better colour than the good glue, but contained a higher percentage of degradation products.

The properties of gelatin are very similar to those of other proteins. It gives the same reactions with Millon's reagent and the biuret test. It is precipitated from its solutions by tannic acid, phosphomolybdic acid and phosphotungstic acid and forms insoluble compounds with formaldehyde. It forms an insoluble compound with picric acid when present in excess, and is precipitated from its solution by chlorine or bromine. Like proteins it is precipitated from its solutions by saturation with ammonium sulphate, zinc or magnesium sulphate. It differs from other proteins in that it is not precipitated by acid mercuric nitrate solution, copper sulphate or potassium ferrocyanide.

Detection of Gelatin.—When no other proteins are present, gelatin may be identified by any of the reactions already mentioned. Other proteins may be removed by warming the solution with a little acid mercuric nitrate solution, made by dissolving 1 grm. of mercury in twice its weight of concentrated nitric acid and diluting the solution with four volumes of water. After the proteins have become coagulated, the mixture is filtered and a cold saturated solution of picric acid is added drop by drop to the clear filtrate ; when gelatin is present a transient precipitate is produced at first which becomes permanent when excess of picric acid is present.

The Evaluation of Glue and Gelatin.—The valuation of glue and gelatin depends upon the results of both chemical and physical tests, the latter being sufficient in many cases. The principal physical tests are :

Water Absorbed.—A small piece of the sample weighing about 5 grms. is suspended in cold water by means of a fine silk thread. After 48 hours the gelatin is removed from the water, the excess water drained off or removed with filter paper, and the jelly weighed. Good gelatin absorbs from five to seven times its weight of water, glues from three to four times their weight. The jelly should be clear, firm and odourless, and the water should not be discoloured. In order to obtain consistent results the test should be carried out at some standard temperature.

Consistency Test.—5 grms. of the gelatin or 10 grms. of the glue are soaked in cold water overnight. The jelly is then melted, made up to 100 c.c. with water, the liquid poured into a beaker or cylindrical pot and allowed to set. After twelve hours the *breaking strength* of the jelly may be determined in the manner described for starch pastes.

The results obtained in this way are not very reliable and many people prefer the "*finger test.*" The jelly is made as just described and at the same time similar jellies with known quantities of a standard gelatin such as Coignet's

Gold Label brand. Suitable quantities of the standard gelatin are 5, 4, 3, 2 and 1 grammes. When all have set, the jelly to be tested is compared with the standards by pressing its surface gently with the tip of the middle finger, and the particular standard jelly found which offers the same resistance as the sample. The consistency of the sample is then expressed as a percentage of the standard. Thus, if 10 grms. of the glue give a jelly having the same consistency as that obtained with 3·5 grms. of the standard, the consistency is said to be 35.

The *Bloom gelometer* is a very accurate apparatus and is used in America. A description of it may be found in the *Industrial Chemist*, 1925, p. 87.

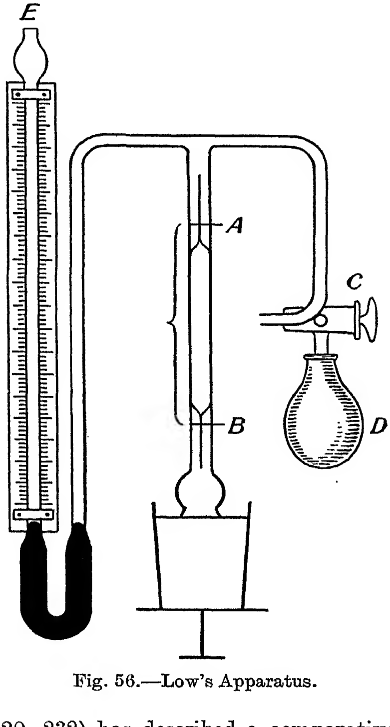


Fig. 56.—Low's Apparatus.

Low (*Analyst*, 1920, 232) has described a comparatively simple apparatus which is capable of giving consistent results. It consists, fig. 56, of a U-tube which has a capillary attachment B, ending in a thistle funnel covered by a rubber membrane, and to which pressure can be applied by a rubber bulb D. The U-tube is charged with mercury, above which is a layer of coloured water. An adjustable scale to indicate pressure is fixed to the limb E. Sufficient water is introduced into the thistle funnel and capillary tube so that when a flat plate is held against the mouth of the former the level of the water will be at the upper mark A, the three-way cock C being open to the air. This cock is then closed to the air and opened to the rubber bulb and scale-limb E, the water in which has been adjusted to the zero mark. A steady pressure is then applied

› the bulb until the water in the capillary falls from A to B, and the level of ıe water in the scale tube is then read. When testing a glue-jelly the container , set so that the surface of the jelly is in contact with the rubber diaphragm, ıe pressure applied, and the reading taken as before. The difference between he pressure recorded and that required to overcome the resistance of the iaphragm alone (obtained in the first experiment) is a measure of the consistency f the jelly.

Melting-point of the Jelly.—When jellies of the same concentration are made ıp with different glues the determination of the melting-point forms a useful ›hysical test. Herold's method (*Analyst*, 1910, 174) is simple: A thermometer ;raduated to tenths of a degree is suspended in the glue solution until the atter sets. The tube containing the jelly is then placed vertically in a water-bath ınd the temperature at which the thermometer sinks through the jelly is taken ıs the melting-point. The *Adhesives Research Committee* (*First Report*, p. 20) ·ecommend the following method: A ten per cent. solution of the glue is prepared n the same way as for the " setting test " (*vide infra*) and poured into a test-tube, ıntil the tube is about two-thirds full. After the jelly has set, a standard steel ball of as large a diameter as possible is placed cautiously upon the surface of the jelly. The tube is fastened to a thermometer and placed in a beaker of water. The water is heated gradually and the temperature at which the ball begins to break the surface of the jelly is regarded as the melting-point.

Setting Test.—According to the *First Report* of the *Adhesives Research Committee*, p. 19, the time taken for a glue-jelly to set gives important indications of the behaviour of the jelly in use. A ten per cent. solution of the glue is prepared by soaking 5 grms. of the sample for 12 hours in 50 c.c. of water. The soaked glue and supernatant liquid are then heated in a thermostat at 37° C., and when complete solution has been obtained, samples are poured into a series of glass cylinders, 0·5 cm. in diameter and 8 cm. in length. These are immersed at once in a thermostat maintained at 20° C., and every few seconds a steel ball of standard size and weight is dropped cautiously into one tube until, finally, the ball is unable to sink more than half-way through the liquid, which is gradually becoming a gel. At this stage successive balls should be dropped into a fresh tube at short intervals. The time from the removal of the tubes from the first thermostat to the setting of the jelly, as indicated above, is recorded by a stop watch and is termed the *setting time*.

Viscosity.—Many people regard the determination of the viscosity of its aqueous solution as the most important physical test in connection with glue or gelatin, since hydrolysis of glutin is detected readily by a decreased viscosity. The determination must be made under standard conditions in order to obtain comparable results. Any of the standard forms of apparatus described in Chapter III may be employed. A 12·5 per cent. solution at 30° C. is used commonly for testing. A special form of viscometer has been adopted by the *American National Association of Glue Manufacturers*, and is described in the *Industrial Chemist*, 1925, p. 86.

Foam Test.—For many purposes it is important that a glue solution should not produce a permanent foam when shaken or agitated. The liability to foam is measured by placing a definite volume (*e.g.*, 100 c.c.) of the solution (at the concentration and temperature required) in a graduated stoppered cylinder, shaking the cylinder continuously for one minute and then measuring the volume of foam produced.

Chemical Analysis.—A common chemical analysis is to determine *moisture*, *ash* and *total nitrogen*. The percentage of nitrogen is multiplied by 5·56 to convert it into *gelatin* (or *glutin*), and the difference between 100 and the sum of the

moisture, ash and gelatin is returned as "*non-gelatinous bodies.*" *Acidity* is determined by soaking a weighed quantity of the sample in cold distilled water for twelve hours, melting the jelly produced, and titrating the acid in the presence of phenolphthalein, calculating the result to sulphuric acid. *Sulphurous acid* is detected and determined in the manner described for wool.

Determination of Fat.—When only *neutral fat* is required, about 5 grms. of the finely powdered glue are extracted with petroleum ether in a Soxhlet extractor in the usual manner for 12 hours. The glue is then re-dried and again powdered, after which the extraction is continued for a further twelve hours. If *total fatty matter* be required, the glue is dissolved in water and digested on the water-bath for some time with hydrochloric acid to decompose soaps. The solution is then dried on sand, the residue powdered finely and extracted in a Soxhlet extractor.

The conversion of the percentage of nitrogen into gelatin does not give information of very much value. In the examples given in the table on p. 230 both the good and poor gelatins contain practically the same percentage of nitrogen, but with the poor gelatin more of it is present as deleterious peptone. The following method of analysis was proposed by the present authors (*J.S.C.I.*, 1904, 1072) with the object of differentiating between the different kinds of nitrogenous compounds present: First the *total nitrogen* is determined. The nitrogen present as *gelatin* is then determined by precipitation with zinc sulphate, the difference between the total nitrogen and the gelatin nitrogen being that present in the form of *peptone* or other *degradation product.* The total nitrogen is determined by the Kjeldahl method in the usual manner; about one gramme of the sample is a suitable quantity to weigh out; the solution should be made up to 250 c.c. and an aliquot portion used for distillation. A second portion of the sample is weighed out, soaked in cold water for some hours and the mixture warmed to dissolve the gelatin. Zinc sulphate is stirred into the solution until the gelatin is completely precipitated. The precipitate is filtered off on a Gooch crucible and washed with a cold saturated solution of zinc sulphate. The asbestos and precipitate are then transferred to a Kjeldahl flask and the nitrogen determined. This multiplied by 5·56 gives the *gelatin.* The difference between this and the product of the total nitrogen multiplied by 5·56 is regarded as *peptone.*

The Diffusible Nitrogen Test.—This test is recommended by the *Adhesives Research Committee* (*First Report,* p. 20). The glue under examination is made into a jelly with water, in such proportions that 2·1 grms. of nitrogen are contained in 75 c.c., approximately 15 grms. of glue being required. This is weighed out and the water is poured on to it. After about 12 hours the mixture is heated to 37° C. for 2 hours, and finally to about 90° C. for 30 minutes. The solution is then poured into a Petri dish (14 cm. in diameter) and allowed to set. 100 c.c. of water are then poured on to the surface of the jelly and the dish is covered and placed in a thermostat at 20° C. for 20 hours. At the end of this time the aqueous phase is poured off and the nitrogen determined by the Kjeldahl method, being expressed as milligrammes of nitrogen per 100 c.c. of aqueous phase. Good skin glues give from 54 to 72 milligrammes, whilst bone glues yield from 13 to 20 milligrammes.

Casein.

Casein is a colourless substance which dissolves in water forming an opalescent viscous solution from which it may be precipitated by alcohol, tannic acid, mercuric and copper salts. Like all proteins it gives a red colour with Millon's

agent and a violet colour with the biuret test. It is soluble in dilute alkalis, om which it may be precipitated by acids. It dissolves also in concentrated drochloric acid, with the production of a violet colour.

Analysis.—The following method of analysis is due to Davies (*Industrial hemist*, 1929, 202): *Moisture, ash* and *nitrogen* are determined in the usual anner. The percentage of nitrogen multiplied by 6·25 gives the *casein* or other otein present. *Fat* is determined by the hydrochloric acid digestion method; weighed quantity of the sample is placed in a small flask with equal volumes water and hydrochloric acid and heated in boiling water until the casein has issolved and the fat floats on the surface of the liquid. The contents of the ask are then washed into a separating funnel and the fat extracted three times ith petroleum ether. The united extracts are evaporated, the residue dried nd weighed.

Other determinations of importance are as follows: *Sugar*—A weighed uantity of the sample is extracted with 50 per cent. alcohol by shaking in a toppered bottle. The mixture is then filtered and the *lactose* determined by neans of Fehling's solution. *Acidity*—About 1 grm. of the casein is placed n a stoppered bottle and 25 c.c. of decinormal sodium hydroxide added. When he casein has dissolved, 100 c.c. of distilled water, free from carbon dioxide, re added, and some phenolphthalein solution. The liquid is then titrated with lecinormal acid. The number of cubic centimetres of $N/10$ alkali used up by ne gramme of casein, free from moisture, fat and ash, is termed the acidity of the sample. Pure casein combines with about 9 c.c. of alkali under these onditions.

Borax Solubility Test.—The casein is ground to pass through a 40-mesh ieve, 15 grms. are weighed into a 250 c.c. beaker and 100 c.c. of a 0·2 M borax solution (76·29 grms. $Na_2B_4O_7 . 10\,H_2O$ per litre) are added with vigorous stirring. The mixture is allowed to stand for 30 minutes, being stirred frequently during the first five minutes, and once every five minutes afterwards. A casein of known purity should be used as a control, the behaviour of both samples being compared, viscosity tests being useful.

Vegetable Gums.

The term gum is applied strictly to the exudations obtained from plants or trees which give mucilaginous colloidal solutions with water, these having adhesive properties. True gums consist principally of arabin, cerasin and bassorin. Certain other vegetable products, such as Irish moss, Iceland moss, gum tragacanth, gum tragasol, agar-agar, algin and pectin are also termed gums, although they do not in all cases contain arabin, cerasin or bassorin, and have little adhesive power.

Arabin, the most important constituent of true gums, is a compound of arabic acid, $C_{12}H_{22}O_{11}$, with calcium and magnesium. It is soluble in cold water, its aqueous solution having a slightly acid reaction and a *laevo*-rotatory action on polarised light. Both *cerasin* and *bassorin* are insoluble in water, but cerasin is changed into arabin by prolonged boiling with water. Both cerasin and bassorin are converted into soluble derivatives by oxidising agents such as hydrogen peroxide in the presence of sodium carbonate, and bassorin is said to give a substance indistinguishable from pectin upon prolonged hydrolysis with acids.

The true gums may be divided into three classes, namely:

(1) Those consisting principally of arabin, such as *gum acacia, gum arabic, gum Senegal* and *Indian gum.*

(2) Gums containing arabin and cerasin, illustrated by *cherry gum*, *plum gum*, *almond gum* and *peach gum*.

(3) Gums which contain but little arabin or cerasin and consist principally of bassorin, such as *gum tragacanth*.

Many of the following details of the analysis of gums are taken from a paper published by the present authors in the *Chemical Trade Journal*, 1928, p. 500.

Gum Arabic.—Commercial samples of gum arabic vary in colour from pale yellow to brown, according to their origin and purity. The gum may be met with in the form of a powder, or small irregular-shaped granules or lumps. It can be pulverised readily and has a specific gravity of from 1·3 to 1·4. The best varieties of the gum, such as are used in medicine, are known as *gum acacia*. Pure gum arabic is completely soluble in water. If an insoluble residue be left it indicates some insoluble adulterant or the presence of another gum containing either cerasin or bassorin. Glycerol dissolves gum arabic completely, but the gum is insoluble in the usual organic solvents.

Gum arabic may be detected by the following tests: It is precipitated from its solutions by adding two volumes of alcohol, and if the solution be acidified, the precipitate contains all the arabic acid present in the gum. Millon's reagent gives a gelatinous precipitate soluble in excess of the reagent. A cold saturated solution of borax or a solution of basic lead acetate produces a colourless gelatinous precipitate and sodium hydroxide a turbidity. When a 30 per cent. solution of gum arabic is shaken with cold Nessler solution, a turbid grey emulsion is formed which changes gradually into a grey precipitate; if the test is made at the boiling-point the precipitate is produced immediately. Sodium hydroxide in the presence of copper sulphate gives a blue precipitate and a colourless supernatant liquid. A neutral solution of ferric chloride precipitates gum arabic completely. Gum arabic contains "oxidases" which give characteristic colour reactions. If one drop of 10-volume hydrogen peroxide solution be added to a mixture of equal volumes of a cold 30 per cent. solution of gum arabic and tincture of guaiacum, a blue colour is produced. Or if the solution be mixed with an equal volume of pyramidon, dimethylaminophenyl-dimethylpyrazolone solution, and 12 drops of hydrogen peroxide added, a blue-violet colour develops in from 5 to 10 minutes.

Analysis.—The general analysis includes the determination of *moisture*, *ash* and *matter insoluble in water*. The moisture content is about 15 per cent., and the ash should not exceed 3 per cent.; the latter consists chiefly of potassium and calcium. When distilled with phosphoric acid and water, the distillation being repeated until no more acid comes over, the volatile acid yielded by 1 grm. of the gum should not require more than 1 c.c. of decinormal sodium hydroxide solution for neutralisation.

The *specific rotation* is of importance. Since genuine gum arabic is always *lævo*-rotatory, any sample which is *dextro*-rotatory must contain dextrin or some other adulterant. Dextrin always contains dextrose. Pure gum arabic does not reduce Fehling's solution; hence any sample which has a reducing action is probably adulterated. The presence of *dextrin* is indicated also by the following tests: If fragments of the solid gum are placed in a Petri dish and covered with ferric chloride solution (sp. gr. 1·48, diluted with an equal volume of water) for one minute, the fragments of gum adhere to the dish when the liquid is poured off, but dextrin passes into solution. When neutral ferric chloride solution is added to a concentrated solution of gum arabic, gelatinisation takes place at once and the jelly is not altered by agitation with water; but if dextrin is present, a cloudy liquid is formed upon the addition of water. If 5 c.c. of a 20 per cent. solution of the gum are shaken with 3 c.c. of a solution of

rric chloride and potassium ferricyanide acidified with hydrochloric acid, a lue colour is produced if dextrin be present.

The fact that different gums require different volumes of alcohol to bring bout their precipitation is often of use in the testing of gum arabic. Some etails are given in the following table:

Concentration of Alcohol.	Gum Precipitated.	Nature of Precipitate.
2 volumes, ...	Gum arabic.	White, flocculent.
,, ...	Gum tragacanth.	Jelly-like.
2·5 volumes, . . .	Indian gum.	Stringy or pasty.
3 volumes, ...	Dextrin.	Fine and sticky.
4 volumes, ...	Agar-agar.	Fine.

Dextrin may be determined quantitatively by means of ferric chloride olution. The aqueous solution of the gum is concentrated to a syrup and reated with 10 volumes of alcohol. The resulting precipitate is collected and lried and 1 grm. of the dry residue dissolved in 10 c.c. of water. This solution s mixed with 30 c.c. of proof spirit, 4 drops of ferric chloride solution containing 6 per cent. of the anhydrous chloride, and a few decigrammes of powdered alcium carbonate. The mixture is stirred, allowed to stand for a short time, nd filtered. The precipitate is washed with proof spirit, redissolved in dilute ydrochloric acid and the gum precipitated by adding excess of alcohol. The recipitated arabic acid is filtered off, dried and weighed. The dextrin is preipitated by adding strong alcohol to the filtrate from the ferric chloride recipitate.

In another method the aqueous solution of the gum is treated with basic ead acetate solution until the gum is just precipitated. The gum is filtered off nd the filtrate treated with sulphuretted hydrogen to precipitate the lead, the ulphide being filtered off. Dextrin is then precipitated by adding five volumes f alcohol to the filtrate.

The detection of *cerasin* and *bassorin* has been mentioned already. Gums which are rich in arabin are dissolved by chloral; those containing cerasin and rabin give a clear solution in from 4 to 5 days, and a mucilage or jelly formed y the swollen cerasin. When much bassorin is present only a swollen cloudy nucilage is produced.

The following method of examination is given by the *Codex Français*: 5 grms. of the gum are soaked in 10 c.c. of cold water for 15 to 20 hours, the mixture being stirred frequently. The solution obtained should be syrupy, nearly colourless, almost transparent and only slightly acid. It should be capable of being filtered through muslin, only traces of tissue remaining, swollen undissolved particles being absent. The solution should give a copious precipitate with an equal volume of alcohol, none with a neutral solution of lead acetate but a white precipitate with the basic salt. To determine *cerasin* and *bassorin*, 40 grms. of the sample are soaked in 500 c.c. of water at 20°–22°C. for 24 hours, diluted with 500 c.c. of water, well mixed and allowed to stand. The clear solution is decanted off, and the insoluble matter removed by filtration and boiled with a ten per cent. solution of sodium carbonate to dissolve cerasin. The solution is filtered, acidified slightly with phosphoric acid and an equal volume of 98 per cent. alcohol added. In the presence of cerasin a white precipitate is produced, which may be filtered off, and weighed. The residue after treatment with sodium carbonate contains any bassorin which may be present.

For the direct determination of gum arabic the method of Waters and Tuttle (*J. Ind. Eng. Chem.*, 1916, **8**, 413) is the most convenient: A solution is made by dissolving 50 grms. of copper acetate in water, adding excess of ammonia and diluting to one litre with water and alcohol in such a manner that 50 per cent. of the latter is present. For each test 50 c.c. of the gum solution (0·25 grm. gum) are mixed with 50 c.c. of alcohol and 25 c.c. of the reagent, the mixture being stirred well. The precipitate is collected on a Gooch filter, washed successively with ammoniacal 50 per cent., 75 per cent. and 95 per cent. alcohol, dried and weighed. The crucible is then ignited and weighed again. The difference between the two weights gives the gum arabic.

Chauvin's method (*J.S.C.I.*, 1912, 197) is specially suitable for the determination of gums in syrups, etc. To 5 c.c. of the syrup are added 5 c.c. of hydrochloric acid and 85 c.c. of absolute alcohol, the acid and alcohol being added drop by drop with constant stirring. The precipitate is filtered off, washed with alcohol containing 10 per cent. of hydrochloric acid, then with absolute alcohol, dried and weighed. The percentage of gum is found by adding 16·1 per cent. to the weight of the precipitate, this representing the average percentage of water plus ash in the original gum.

Rocques and Sellier (*J.S.C.I.*, 1911, 823) treat 25 grms. of the syrup with 80 c.c. of 90 per cent. alcohol, the first portions being added drop by drop with vigorous stirring; then 2 c.c. of a saturated alcoholic solution of lead acetate are added and the whole well shaken. Alternatively, 20 c.c. of the syrup are treated with 10 c.c. of water and 2 c.c. of saturated alcoholic lead acetate solution, followed, after shaking, by 90 c.c. of 95 per cent. alcohol. After standing for 20 minutes the precipitate is filtered off, washed with 75 per cent. alcohol, dried and weighed. It is then ignited with fuming nitric acid and weighed again. The difference between the two weights gives the true gum, and this multiplied by $\frac{100}{85}$ the actual gum.

The valuation of a gum for adhesive purposes in the absence of impurities chiefly depends upon physical tests.

Fromm's method of examination (*Zeitsch. anal. Chem.*, 1901, **40**, 143-168) is as follows: A solution is prepared having a specific gravity of 1·035 at 15° C., which corresponds to about 10 per cent. air-dried gum or 8·5 per cent. of anhydrous substance. An average sample of about 50 grms. is powdered coarsely and shaken at intervals in 200 c.c. of water. The mixture is allowed to stand overnight, then filtered through muslin into a 500 c.c. cylinder and diluted with water to the specific gravity of 1·035. The following tests are made with this solution:

Frothing Power.—This is measured by shaking a measured volume of the solution in a stoppered graduated cylinder and reading off the volume of the foam produced.

Insoluble Matter.—The insoluble matter on the filter is washed into a graduated cylinder, allowed to settle and its volume measured.

Viscosity.—This is determined by means of Engler's viscometer at 20° C. and compared with that of water.

The Acid Value is determined by titration of the aqueous solution with decinormal sodium hydroxide solution and expressed as milligrammes of sodium hydroxide required to neutralise one gramme of the gum.

Rotatory Power.—The best varieties without exception give a negative reading when examined in a 100 mm. tube.

Tenacity.—Dalen's method is recommended. The mean breaking strength

d elasticity of a suitable absorbent paper are determined and also the mean ight of strips 18 cm. × 15 cm. under average moisture conditions (65 per nt.). Pieces of this paper are placed on a solution of gum spread on a glass ate, and after removing the excess of gum, dried in an atmosphere containing per cent. of moisture. When dry, 20 strips are cut from the gummed paper id the breaking strain again determined. The quantity of gum present in e paper is determined by weighing the strips. The *adhesive power* is obtained multiplying the breaking weight in grammes by 1,000, or by the number millimetres width of a sheet of paper one metre long and one metre wide, id dividing by the product of the width in millimetres of the strip tested and e weight in grammes of a square metre of the paper.

The apparatus of Schopper is used commonly for determining the *breaking rain* of the strips.

In addition to the acid value given by Fromm the "volatile acid" and saponification equivalents" should be determined also.

The *volatile acid* is determined by distilling the aqueous solution with hosphoric acid until only a little is left. After cooling, more water is added nd the distillation continued, this being repeated until no more acid comes ver. The combined distillates are then titrated with decinormal sodium ydroxide. The results are expressed as cubic centimetres of alkali required y one gramme of the gum. The following are examples :

Gum arabic, .	1 c.c.
Gum tragacanth,	3 c.c.
Indian gum, .	10 to 20 c.c.

The *saponification equivalent* denotes the number of milligrammes of sodium hydroxide required to saponify one gramme of the gum. A measured volume of the solution is neutralised towards phenolphthalein with decinormal sodium hydroxide. A measured excess of the alkali is then added and the mixture boiled gently under a reflux condenser for an hour. After cooling, the unused sodium hydroxide is determined by titration.

Gum Tragacanth.—This gum is an exudation of the *astragalus gummifer*. It occurs in lumps, filamentous or foliaceous strips or irregular-shaped granules. There are many varieties, but the Smyrna gum is the best. Good samples are colourless or pale yellow, but the colour of the lower-grade products may be brown or even black. Gum tragacanth is very hard and is difficult to pulverise, differing in these respects from gum arabic and other similar gums.

When gum tragacanth is soaked in water, part of it is dissolved and the remainder swells up, forming a thick mucilage. The soluble portion consists of arabin ; the insoluble residue contains bassorin and other insoluble bodies. When examined under the microscope gum tragacanth is seen to contain broken-down cell structures and starch granules. The composition is variable ; the following figures were obtained by the analysis of three commercial samples :

	1	2.	3.
	Per cent.	Per cent.	Per cent.
Moisture, ...	13·95	17·70	23·72
Ash, ...	1·93	3·37	5·85
Soluble arabin, ...	20·00	12·50	14·08
Insoluble bassorin, ...	64·12	66·43	56·35

All three samples gave the reactions of the pure gum. The bassorin may be rendered soluble by heating it with alkalis, especially in the presence of oxidising agents.

Gum tragacanth gives about one per cent. of volatile acid when distilled with phosphoric acid and has a saponification value of from 100 to 180. When heated with sodium hydroxide solution a yellowish-brown colour is produced. It does not contain oxidases. It is capable of taking up as much as 50 times its weight of water. It is precipitated by adding two volumes of alcohol, forming jelly-like clots which float in the middle part of the solution, whereas gum arabic comes down as a flocculent precipitate. It gives a precipitate with normal or basic lead acetate, ammonium sulphate and ammonium oxalate, but none with ferric chloride or borax. Gum tragacanth is not often adulterated with other gums, although gum arabic, cherry or a similar gum or Indian gum might be used.

The following tests, given by de Keghel (*Fabrication des Colles*), may be applied to determine the purity of the gum: 1 grm. of the gum when soaked in 50 c.c. of water should give a firm opalescent homogeneous mucilage, free from cell débris. Indian gum produces a mucilage containing reddish particles in suspension. When 1 grm. of borax is added to a 2 per cent. solution of the gum the mixture should remain clear and should not become liquid in 24 hours. When 1 grm. of the gum is heated with 20 c.c. of water until completely gelatinised, then treated with 5 c.c. of hydrochloric acid and heated again for five minutes, no colour should be produced, a rose colour indicating the presence of Indian gum. The *volatile acid* figure should not be more than 3 c.c. and the *saponification equivalent* not less than 100. The aqueous solution should be nearly neutral. When 1 grm. of the gum is ground with 1 c.c. of glycerol, 48 c.c. of water added and the whole mixed, a consistent jelly should be produced which is capable of forming drops requiring at least ten seconds to fall from a glass rod. The *viscosity* is determined in the following manner: 1 grm. of the gum is agitated with 2 c.c. of alcohol in a 100 c.c. flask, made up to the mark with water and allowed to stand for 24 hours with frequent shaking. The viscosity is then measured. In a good sample the number of drops formed in two minutes should not be more than 30.

When a small quantity of the powdered gum is mixed with strong sulphuric acid, no colour should be produced in one minute and only a brown colour in one hour. The *Codex français* gives the following method of testing: 1 grm. is macerated for 24 hours with 100 c.c. of water; an opaque liquid mucilage should be formed containing fragments of swollen gum; this is filtered through paper. The insoluble residue should give a blue colour with iodine, but no starch should be present in the filtrate. To test for *gum arabic* two volumes of alcohol are added to the filtrate and the nature of the precipitate is observed as already described. When less than 10 per cent. of gum arabic is present this test fails and the following is substituted: 20 grms. of the gum are macerated for 24 hours with 100 c.c. of water and 5 drops of tincture of guaiacum are added. If four per cent. of gum arabic be present a blue colour is produced in 10 minutes, but with smaller quantities as long as six hours may be necessary.

Agar-agar.—Agar is prepared from various seaweeds in Japan, Hong Kong and Australia. It is sold either in the form of a powder or in long flat strips. When treated with cold water it swells up like gelatin, but when the swollen mass is heated with water it does not dissolve until a temperature of over 85° C. is reached. When the solution is cooled a firm jelly is formed which melts at about 85° C. The jellying power of agar is very marked, so little as 0·5 per cent. being sufficient to form a gel. The composition of commercial agar is rather

ariable, but it contains 1–2 per cent. of a protein and gives 90 per cent. of oluble extract. The protein is probably an impurity. When agar is hydrolysed y acids, arabinose, galactose and methyl pentoses are produced; according o Fairbrother and Mastin (*Chem. Soc. Trans.*, 1923, **123**, 1412-1424), agar-agar onsists principally of the calcium salt of an acid sulphuric ester which is onsidered to be ionised in the sol and gel states, a reversible reaction of the ype

$$(RO \cdot SO_2 \cdot O)_2Ca + 2\,HCl \rightleftharpoons 2\,RO \cdot SO_2 \cdot OH + CaCl_2 \ .$$

being established.

The free acid swells less in water than the calcium salt and its ionisation and swelling are diminished further by the presence of another acid, reaching a maximum in dilute alkali. The calcium can be removed by soaking alternately in water and $N/100$ hydrochloric acid. The corresponding potassium salt forms a very firm gel. Agar-agar behaves differently from gelatin as regards its swelling with acids and alkalis. The swelling in mineral acids decreases almost as a linear function of the negative logarithm of the hydrogen-ion concentration. In sodium hydroxide the relative swelling shows a maximum greater than that in water; the swelling in water is however greater than that in baryta solution. The swelling in ammonia is greater than that in sodium hydroxide solution, both maxima occurring at the same pH value.

The detection of agar-agar is difficult, especially as the substance is used frequently in such things as jam, which contain pectin or gelatin. It can be separated from the latter by means of tannic acid, since it does not give an insoluble tannate. Pectin may be precipitated from an acetic acid extract by adding calcium chloride, since the calcium salt is insoluble; the agar remains in solution. Advantage may be taken also of the fact that whilst gelatin and other substances such as pectin dissolve in water at 50° C., agar dissolves only at a temperature of 85° C. or over. A solution of agar is not precipitated by alcohol until nearly four volumes have been added and then a finely divided precipitate appears which settles very slowly. According to Cook and Woodman (*J. Ind. Eng. Chem.*, 1918, **10**, 530), the separation of agar and other vegetable gums in fruit products may be effected in the following manner: The sample is diluted with water and heated for 5 minutes with 5 c.c. of dilute acetic acid and 25 c.c. of a 10 per cent. tannin solution, centrifuged to precipitate casein and coagulate proteins, fats and gelatin. The precipitate is removed and the filtrate again heated with 40–50 c.c. of the tannin solution and centrifuged to precipitate the remainder of the proteins. The clear filtrate is treated with twice its volume of acetone, centrifuged and filtered, the filtrate being discarded. The absence of any precipitate indicates that no gums, dextrins or milk solids are present. If a precipitate is formed it is dissolved in 50 c.c. of warm water, the solution slightly acidified with acetic acid, 10 c.c. of ammonia (sp. gr. 0·9) added and the mixture centrifuged and filtered. The precipitate, which may consist of calcium phosphate derived from milk, is discarded. The filtrate is made slightly acid with acetic acid and alcohol is added, one volume at a time, until a well-defined precipitate appears. When no precipitate is produced with five volumes of alcohol gums and dextrin are absent. With about two volumes of alcohol gum arabic and gum tragacanth come down, the former as a white flocculent precipitate, which settles quickly and is neither coherent nor sticky, but becomes dry and powdery on pouring off the alcohol and exposing to air. Gum tragacanth forms a jelly-like mass, floating in clots in the upper layers of the mixture, flattening down after standing in air and forming a semi-transparent coherent layer. Indian gum is not precipitated

until two and a half volumes of alcohol have been added; it forms a stringy precipitate, becoming very coherent after settling, and darkening and forming a tough coherent layer on exposure to the air. Dextrin comes down as a fine precipitate when three volumes of alcohol have been added; this precipitate is very sticky and settles slowly, becoming hard upon prolonged exposure to the air. Agar-agar does not come down until nearly four volumes of alcohol have been added. It may be identified by the presence of characteristic *diatoms*, which are detected by microscopic examination.

Indian gum may be identified by its high volatile acidity. An aqueous solution of the gum is distilled with phosphoric acid two or three times or until no more acid comes over. The distillate is then titrated with decinormal sodium hydroxide solution in the presence of phenolphthalein. The results obtained with some different gums are given in the following table:

Gum.	*N*/10 Alkali Required by 1 grm.
Indian gum, . . .	10–20 c.c.
Gum arabic, . . .	less than 1 c.c.
Dextrin, . . .	do.
Gum tragacanth, . .	3 c.c.

Gum tragacanth is characterised by having a high saponification value, viz., 100–180. This is determined by boiling a neutralised aqueous solution of the gum with a known volume of standard sodium hydroxide solution, cooling and titrating-back with acid. The detection of gum arabic has already been dealt with.

Quantitative Determination.—This depends upon the observation of Fairbrother and Mastin that agar contains a sulphonic acid grouping, $R{<}{\substack{O\,.\,SO_2\,.\,O\\O\,.\,SO_2\,.\,O}}{>}Ca$, similar to that found by Haas in Irish moss. The following method is due to King (*Analyst*, 1925, 371): 100 grms. of the material containing the agar, such as jam, are freed from sugars by means of alcohol and precipitation by the method of Haynes and Carré described for pectins. The residue on the Buchner filter is boiled for some minutes with 200 c.c. of water, filtered, washed, re-boiled and re-filtered, pressure being used if required. It is essential to keep the temperature of the liquid above 80° C. during filtration. The filtrate is concentrated to 300 c.c. and 100 c.c. are taken for determination of the *free sulphate*. The sulphate is determined by precipitation with barium chloride solution, but hydrochloric acid should not be added until the last moment, to avoid decomposing the agar. The remaining 200 c.c. are concentrated to 100 c.c. and an equal volume of concentrated hydrochloric acid is added. The mixture is boiled for six hours, the water lost by evaporation being replaced from time to time. The liquid is then concentrated to 25 c.c., diluted to 300 c.c. and filtered whilst still hot. Barium chloride solution is added and the mixture allowed to stand overnight, after which the barium sulphate is filtered off and weighed. This gives the *total sulphate*, that is the sum of the free sulphate and that produced by decomposition of the sulphonic acid. The results are calculated from the formula

$$\text{Weight of agar} = 15\,[\tfrac{3}{2}\,(a - 2\,b)],$$

where a = total $BaSO_4$ from the 200 c.c.

b = $BaSO_4$ from free sulphates in the 100 c.c.

15 represents rather less than the maximum $BaSO_4$ obtained by hydrolysis and precipitation from agar-agar.

Irish Moss or *Carraghen*.—This, like agar-agar, is a seaweed collected principally in Ireland. The plant is merely dried and forms yellowish-brown crinkled fragments with an odour reminiscent of seaweed. The dry weed contains about 60 per cent. of matter soluble in water, which includes a carbohydrate, a nitrogenous substance and a pectin. When digested with hot water, intensely mucilaginous solutions are obtained. These have great emulsifying power, but no adhesive properties. The solution gives precipitates with alcohol and lead acetate, but no coloration with iodine. A solution of Irish moss is used as an emulsifier in the preparation of cod liver oil emulsions and also to a certain extent in the finishing of cotton goods, since it produces a soft and bulky handle which is not sticky. The mucilage is prepared either by boiling the moss with water alone or with water containing a little alkali. About 10 kilos. of the moss are soaked in 150 litres of hot water until the moss becomes swollen. A little sodium hydroxide or sodium carbonate solution is then added and the mixture boiled gently until no more is dissolved. The mixture is then filtered through muslin, the residue boiled again with water and filtered, the combined filtrates being diluted to about 350 litres.

Irish moss should contain from 1·5 to 2·5 per cent. of nitrogen. Haas and Russell Wells (*Analyst*, 1927, 265) have showed that it contains an "ether" sulphate of the type

$$R{<}\begin{matrix}O\,.\,SO_2\,.\,O\\O\,.\,SO_2\,.\,O\end{matrix}{>}Ca,$$

similar to that found in agar-agar.

Determination.—The method described for the analysis of agar may be used for the determination. Haas and Russell Wells (*loc. cit.*) proposed the following method of analysis: A measured volume of the solution, containing approximately 0·2 grm. of dry extract, is diluted to 100 c.c., acidified with a few drops of 4 N hydrochloric acid and treated with 150 c.c. of a solution of benzidine chloride containing 4 grms. of benzidine and 5 c.c. of concentrated hydrochloric acid in two litres. After standing for 20 minutes the precipitate is filtered off and washed with a saturated aqueous solution of benzidine sulphate until free from chlorine. The filter paper and precipitate are then put into a beaker, 250 c.c. of water added, the contents of the beaker heated to 80° C. and titrated with $N/10$ sodium hydroxide solution, phenolphthalein being used as indicator. 1 c.c. $N/10$ NaOH $\equiv$ 0·0324 grm. mucilage. The pectin may be estimated by the methods already described.

Iceland Moss.—This consists of a dried lichen known as *cetraria islandica*. When boiled with water containing a little sodium carbonate, about 60 per cent. of the moss is dissolved, the solution forming a jelly when cold. The insoluble residue is hydrolysed when boiled with dilute acids, giving dextrose, galactose and a little mannose. According to Hesse (*J.S.C.I.*, 1917, 566) when Iceland moss is extracted with ether, proto-α-lichesteric acid is dissolved. Acetone extracts the potassium salt of fumaroprotocetraric acid, which is readily split up into acid potassium fumarate and cetraric acid. Cold water extracts carbohydrates, including lichenin, $C_6H_{10}O_5$, *d*-lichenidin and lichenoin, $C_{12}H_{20}O_{10}$, which, when hydrolysed gives dextrose and a carbohydrate, $C_6H_{10}O_5$, yielding a crystalline compound with barium hydroxide.

CHAPTER XVI.

METALLIC SALTS.

Alkali Metals.

Sodium Chlorate, $NaClO_3$.—The detection and determination of chlorates in bleaching powder has been described already. The analysis of sodium chlorate may be made in two ways. The general method is to distil the salt with hydrochloric acid, pass the chlorine which is given off into a solution of potassium iodide, and determine the iodine liberated by means of sodium thiosulphate solution. The reaction is represented by the equation

$$NaClO_3 + 6\,HCl = NaCl + 3\,H_2O + 3\,Cl_2.$$

$$\text{Since } NaClO_3 \equiv 6\,Cl, \quad \therefore\ 127 \text{ parts of iodine} \equiv \frac{NaClO_3}{6}.$$

About 0·3 grm. of the chlorate is placed in a flask together with 25 c.c. of pure hydrochloric acid. The flask is connected to a U-tube containing potassium iodide solution, immersed in cold water. The contents of the flask are warmed gently to expel the chlorine, and finally boiled. All the corks used should have been soaked previously in paraffin wax.

Another method depending upon the oxidation of ferrous sulphate is as follows: A weighed quantity of the chlorate is dissolved in water and the solution diluted to a known volume. A portion of this solution is placed in a flask provided with a Bunsen valve and the air is expelled by means of carbon dioxide. A known excess of decinormal solution of ferrous sulphate containing excess of sulphuric acid is added and the mixture boiled gently for about 10 minutes. The liquid is then cooled and diluted, and the ferrous iron titrated with decinormal permanganate using the method of Zimmermann-Reinhardt. Potassium permanganate cannot be used in the ordinary way in the presence of hydrochloric acid or chlorides since chlorine would be liberated, but when manganous sulphate is added and the permanganate solution is run in slowly, accurate results can be obtained. The manganous solution is prepared by dissolving 67 grms. of crystalline manganous sulphate, $MnSO_4 . 4\,H_2O$, in 500 c.c. of water, adding 138 c.c. of phosphoric acid (sp. gr. 1·7) and 130 c.c. of concentrated sulphuric acid and diluting the mixture to one litre. For each titration 10 c.c. of this solution are required. The action of ferrous sulphate on sodium chlorate is represented by the equation

$$NaClO_3 + 6\,FeSO_4 + 3\,H_2SO_4 = NaCl + 3\,Fe_2(SO_4)_3 + 3\,H_2O.$$

The value of the ferrous sulphate solution in terms of potassium permanganate is determined by a blank test. If t_1 and t_2 represent the permanganate solution used in the blank and chlorate tests respectively, then $t_1 - t_2$ is the equivalent of the sodium chlorate present in the volume of the solution used, and if x be

the weight of commercial sodium chlorate present in one litre of the solution and 10 c.c. were used for the titration, then

$$\frac{17 \cdot 75\,(t_1 - t_2)}{x} = \text{per cent. pure } NaClO_3 \text{ in sample.}$$

Sodium chlorate may contain both *perchlorate* and *chloride* as impurities. These can be determined in the following manner: A solution of the substance is made. The chlorine as chloride is determined in one portion by means of silver nitrate. A second portion is boiled with ferrous sulphate solution to reduce the chlorate to chloride, acidified with nitric acid and the chloride again determined. Another portion is evaporated to dryness, mixed with ammonium chloride and ignited carefully in a platinum dish covered with a clock glass. This changes both chlorates and perchlorates into chlorides. The total chlorides may either be weighed in the dish or precipitated by means of silver nitrate. It is important that the sodium chloride should not be heated too strongly, for not only is it somewhat volatile, but it may also damage the dish.

Sodium Chloride, $NaCl$.—Commercial sodium chloride may contain small quantities of sodium sulphate and also moisture and insoluble matter. *Moisture* is determined by heating a weighed quantity of the sample to a temperature of about 120° C. until it is constant in weight. *Insoluble matter* such as dirt is separated by dissolving the salt in water and filtering the solution through a weighed Gooch crucible. The filtrate should give only faint reactions for *sulphates*; calcium, magnesium and iron should be absent. The proportion of the salt is determined either by titration with decinormal silver nitrate solution or by precipitation in a solution acidified with nitric acid and collecting the silver chloride on a weighed Gooch crucible. Chlorides may be determined also by titration with potassium sulphocyanide solution or Voteck's solution, as described in Chapter IV. The concentration of a solution of the salt may be estimated approximately from its specific gravity by reference to the following table:

SPECIFIC GRAVITY OF SODIUM CHLORIDE SOLUTIONS.

Sp. Gr. at 15° C.	Percentage of Salt.	Sp. Gr. at 15° C.	Percentage of Salt.
1·0072	1	1·1038	14
1·0145	2	1·1115	15
1·0217	3	1·1194	16
1·0290	4	1·1273	17
1·0362	5	1·1352	18
1·0437	6	1·1431	19
1·0511	7	1·1510	20
1·0585	8	1·1593	21
1·0659	9	1·1675	22
1·0733	10	1·1758	23
1·0809	11	1·1840	24
1·0885	12	1·1923	25
1·0962	13	1·2009	26

Sodium Nitrite, $NaNO_2$.—Lunge's method of analysis is simple and reliable: A weighed quantity of the nitrite is dissolved in water and the solution made up to a definite volume. A measured volume (*e.g.* 50 c.c.) of decinormal potassium permanganate solution is placed in a flask together with about 100 c.c. of 10

per cent. sulphuric acid, the mixture diluted to 400 c.c. and warmed to about 40° C. The sodium nitrite solution is now run into the acidified permanganate solution from a burette, a little at a time, rotating the flask after each addition. The end-point is the decolorisation of the permanganate solution, indicating completion of the reaction

$$2\ KMnO_4 + 5\ HNO_2 + 4\ H_2SO_4 = 2\ KHSO_4 + 2\ MnSO_4 + 5\ HNO_3 + 3\ H_2O.$$

Towards the end of the titration the nitrite solution must be added slowly, as the decomposition of the permanganate solution proceeds slowly. If preferred, an excess of potassium permanganate solution may be added and the excess titrated-back with decinormal oxalic acid, but the method is not so good as the former. 1 c.c. $N/10$ $KMnO_4 \equiv 0{\cdot}0069$ grm. $NaNO_2$. Commercial sodium nitrite should contain 97 per cent. of $NaNO_2$.

Sodium Sulphate, Na_2SO_4.—There are two forms of commercial sodium sulphate, viz.: Glauber salt, $Na_2SO_4 . 10\ H_2O$, and salt cake, which contains from 90 to 95 per cent. of the anhydrous sulphate, Na_2SO_4. The chief impurities are *sodium chloride, sulphates of calcium and magnesium, bisulphates of sodium and iron.* The presence of bisulphate is indicated by an acid reaction and the quantity present may be determined by titration. The other impurities are determined in the usual manner. The sodium sulphate is deduced from the weight of barium sulphate obtained when the sample is treated with barium chloride solution, due allowance being made for any SO_4 present as bisulphate.

$$BaSO_4 \times 0{\cdot}6087 = Na_2SO_4,$$
$$BaSO_4 \times 1{\cdot}3803 = Na_2SO_4 . 10\ H_2O.$$

Analysis.—About 5 grms. of the sample are weighed out, dissolved in distilled water and the solution made up to a definite volume, *e.g.* 250 c.c. A portion of the solution is titrated with sodium hydroxide in the presence of phenolphthalein and the *acidity* calculated to *sodium bisulphate.* A second portion is diluted with water, a little hydrochloric acid added and the solution treated at the boiling-point with excess of barium chloride solution. After standing for about six hours, the *barium sulphate* is filtered off, washed, ignited and weighed.

The following method (Besombe, *Bull. de la Soc. Chim. Belg.*, 1928) is reliable: If to a solution containing sodium chloride, sulphuric acid, sulphates of iron, aluminium, calcium, magnesium and sodium, is added in sufficient quantity a known number of c.c.'s of a standardised solution of sodium carbonate, the small quantities of the ions Fe^{+++}, Al^{+++}, Ca^{++} and Mg^{++} are completely precipitated in the form of insoluble carbonates, and the free acid is neutralised. The filtered solution containing a slight excess of sodium carbonate, after exactly neutralising with sulphuric acid, will contain, after evaporation to dryness and calcining at a dark red heat, the true amount of sodium sulphate, plus the weight of sodium chloride and sodium sulphate resulting from the completed transformation of the sodium carbonate added.

The actual method is as follows: Into a 100 c.c. flask are introduced 30 c.c. of moderately warm water, then 2 grms. of sodium sulphate, finely pulverized. After solution 10 c.c. of $N/10$ solution of sodium carbonate are added (a sufficient quantity in the majority of cases). The solution is then diluted to 100 c.c. with distilled water and filtered through a folded filter. The filtrate is collected in a dry flask. Exactly 50 c.c. are taken in a tared porcelain or platinum crucible and neutralised with $N/5$ sulphuric acid in the presence of methyl orange. This solution is evaporated on a water-bath, then on a sand bath, the residue finally being heated for a few seconds to a dark red heat to destroy organic

matter, cooled and weighed. The sodium chloride present and the sodium sulphate added are subtracted from the weight of the residue to give the weight of sodium sulphate originally present.

Sodium Bisulphate, $NaHSO_4$, when dissolved in water, reacts as though it were decomposed in accordance with the equation

$$2\,NaHSO_4 = Na_2SO_4 + H_2SO_4.$$

A weighed quantity of the salt is dissolved in water and the solution diluted to a definite volume. One portion of the solution is titrated with decinormal sodium hydroxide, in the presence of phenolphthalein (1 c.c. $N/10$ $NaOH \equiv$ 0·0120 grm. of $NaHSO_4$). Another portion is treated with barium chloride, the barium sulphate filtered off and the weight of the precipitate multiplied by 0·5141, giving the sodium hydrogen sulphate present, which should agree with that found by titration if no neutral sulphate is present.

Sodium Acetate, $CH_3COONa\,.\,3\,H_2O$.—Sodium acetate should be neutral to litmus and free from such impurities as iron, chlorides, sulphates, calcium and magnesium, or mineral acids. Since the sodium salts of organic acids yield sodium carbonate quantitatively when ignited, the purity of a sample of sodium acetate may be ascertained by ashing a known weight of the substance at a low temperature, dissolving the ash in water and titrating the solution with decinormal acid in the presence of methyl orange. Each cubic centimetre of acid used corresponds to 0·006 grm. of acetic acid.

The usual method of analysis is to distil off and titrate the acetic acid. For this purpose a weighed quantity of the acetate is placed in a distilling flask together with a little water and a slight excess of phosphoric acid or sodium bisulphate. The liquid is then distilled nearly to dryness, a spiral condenser being used to condense the distillate. The contents of the flask are allowed to cool, a little more water is added and the mixture again distilled, this being repeated until no more acid comes over. The united distillates are then titrated with decinormal sodium hydroxide, phenolphthalein being used as indicator. Sodium acetate, $CH_3COONa\,.\,3\,H_2O$ gives 44·12 per cent. of acetic acid.

Sodium Phosphate, $Na_2HPO_4\,.\,12\,H_2O$, dissolves readily in water, its aqueous solution being alkaline to litmus and methyl orange. When treated with an acid, sodium dihydrogen phosphate is first formed, which is neutral to methyl orange. Hence, if a solution of the phosphate be titrated with decinormal sulphuric acid in the presence of methyl orange, the end-point of the reaction corresponds to the equation

$$2\,Na_2HPO_4 + H_2SO_4 = 2\,NaH_2PO_4 + Na_2SO_4.$$
$$i.e.,\ H_2SO_4 \equiv 2\,Na_2HPO_4\,.\,12\,H_2O,$$
$$\text{or 1 c.c. } N/10 \text{ acid} \equiv 0{\cdot}0358 \text{ grm. } Na_2HPO_4\,.\,12\,H_2O.$$

The percentage of phosphoric acid (P_2O_5) present may be determined gravimetrically by precipitation either as magnesium ammonium phosphate or as ammonium phosphomolybdate.

Magnesium Ammonium Phosphate Method for Phosphate.—The solution of the phosphate is acidified with hydrochloric acid and an excess of magnesia mixture and from 10 to 20 c.c. of a saturated aqueous solution of ammonium chloride are added. The mixture is heated to the boiling-point and 2·5 per cent. ammonia solution added with stirring until a precipitate begins to be formed. The ammonia is then added at the rate of about four drops a minute, this ensuring the formation of a crystalline precipitate, $MgNH_4PO_4\,.\,6\,H_2O$. If the precipitate is not crystalline it should be redissolved in hydrochloric

acid and reprecipitated. When precipitation is complete and the liquid smells of ammonia, the mixture is cooled and about one-fifth of its volume of strong ammonia added. After standing for a short time the precipitate is filtered off on a weighed Gooch crucible and washed with a 2·5 per cent. solution of ammonia. It is finally moistened with a saturated solution of ammonium nitrate made alkaline with ammonia and dried. The crucible is then ignited, at first very carefully and then strongly, to convert the magnesium ammonium phosphate into magnesium pyrophosphate, $Mg_2P_2O_7$. The crucible is cooled and weighed. ($Mg_2P_2O_7 \times 0{\cdot}6379 = P_2O_5$.) Sodium phosphate, $Na_2HPO_4 . 12\ H_2O$, contains 19·83 per cent. of phosphoric anhydride, P_2O_5.

Ammonium Molybdate Method.—When a solution containing phosphoric acid is treated with ammonium molybdate in the presence of excess of nitric acid and ammonium nitrate, a yellow crystalline precipitate of ammonium phosphomolybdate is formed, which has the composition $(NH_4)_3PO_4 . 12\ MoO_3 . 2\ HNO_3 . H_2O$. The solution must be free from silicic acid and organic matter, and should contain very little chloride. The precipitate of ammonium phosphomolybdate is filtered off, washed with dilute nitric acid, redissolved in ammonia and the solution treated with magnesia mixture. The precipitated magnesium ammonium phosphate is weighed as pyrophosphate as in the previous method. The molybdic acid reagent is prepared in the following manner. 125 grms. of powdered molybdic acid are mixed with 100 c.c. of water in a litre flask and 300 c.c. of 8 per cent. ammonia are added gradually, the flask being rotated meanwhile. When the molybdic acid has dissolved, 400 grms. of ammonium nitrate are added to the solution. The solution is then diluted to one litre with distilled water and poured into a litre of nitric acid (sp. gr. 1·19). The mixture is kept at a temperature of about 35° C. for 24 hours and then filtered.

The solution to be tested should not contain more than 0·4 grm. of phosphoric acid, preferably from 0·1 to 0·3 grm. From 100 to 150 c.c. of the molybdic acid solution are added and the mixture heated on a water-bath to a temperature of 70° C., after which it is allowed to cool. The precipitate is filtered off and washed with 1 per cent. nitric acid. The filtrate and washings are allowed to stand for some hours in a warm place in case the whole of the phosphoric acid has not been precipitated. The precipitate is then dissolved in 2 per cent. ammonia, about 100 c.c. being used for both solution and washing. The ammonia solution is raised to the boiling-point, then removed from the source of heat and 15 to 20 c.c. of magnesia mixture added drop by drop with constant stirring, the stirring being continued at intervals until the mixture is cold. After four hours the precipitate is filtered off on a weighed Gooch crucible and washed with 2 per cent. ammonia solution until free from chloride, but the filtrate and washings should not exceed 200 c.c. The precipitate is then dried, ignited and weighed as magnesium pyrophosphate.

Sodium Arsenate, $Na_2HAsO_4 . 12\ H_2O$.—Arsenic acid may be determined by titration with iodine if first reduced to arsenious acid, or gravimetrically by precipitating it as magnesium ammonium arsenate and either weighing this or converting it into the pyroarsenate, $Mg_2As_2O_7$. Sodium metabisulphite is a suitable reducing agent for the volumetric process. The solution of the arsenate is acidified and about 1 grm. of the metabisulphite added. After standing for some time the solution is boiled gently until the sulphur dioxide has been completely expelled. It is then cooled and titrated with decinormal iodine solution. Each cubic centimetre of $N/10$ iodine solution used corresponds to 0·00575 grm. of arsenic pentoxide, As_2O_5. Arsenites may be determined by direct titration of the original solution with iodine and, if present, must be

allowed for. The gravimetric method has been described under the determination of phosphorus.

Potassium Permanganate.—About 3·2 grms. of the powdered sample are weighed out, dissolved in water and the solution made up to one litre, thus producing an approximately decinormal solution. This is titrated with a decinormal solution of oxalic acid. A suitable volume, *e.g.* 25 c.c. of the oxalic acid solution is placed in a flask or beaker together with 20 c.c. of a 20 per cent. solution of sulphuric acid. The mixture is heated to about 60° C. and the potassium permanganate solution run in from a burette until a permanent pink colour is obtained. The decolorisation of the permanganate solution is slow at first, but when the reaction has once started it proceeds rapidly. The reaction is in accordance with the equation

$$2\,KMnO_4 + 5\,(COOH)_2 + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

Hence 1 c.c. $N/10$ oxalic acid solution $\equiv$ 0·00316 grm. permanganate.

Potassium permanganate may be determined also by titration with a decinormal solution of sodium thiosulphate after adding excess of potassium iodide and acidifying, the process being based upon the equation

$$2\,KMnO_4 + 10\,KI + 16\,HCl = 12\,KCl + 2\,MnCl_2 + 8\,H_2O + 5\,I_2.$$

About 2 grms. of potassium iodide are dissolved in a little water in a stoppered bottle, a little dilute acid added and 25 c.c. of the permanganate solution run in. The solution is then diluted to about 250 c.c. and the liberated iodine determined by titration with sodium thiosulphate solution.

1 c.c. $N/10$ sodium thiosulphate solution $\equiv$ 0·00316 grm. permanganate.

Lead.

Lead Acetate, $(CH_3COO)_2Pb \cdot 3\,H_2O$, is the only salt of lead which is used to any extent. It may contain *basic acetate* as an impurity. The *lead* is determined in the following manner: A weighed quantity of the salt is dissolved in water and sulphuric acid is added to precipitate the lead as sulphate. The beaker containing the precipitate is allowed to stand for 12 hours. The lead sulphate is then filtered off on a weighed Gooch crucible, washed with one per cent. sulphuric acid, ignited at a low temperature to drive off the excess of acid and weighed. ($PbSO_4 \times 1{\cdot}2508$ = lead acetate.)

Colorimetric Determination of Lead.—Small quantities of lead are estimated by a colorimetric method. The following solutions are required: (*a*) A standard stock solution of lead containing 0·001 grm. Pb per c.c., made by dissolving 1 grm. of pure lead foil in nitric acid, evaporating the solution to dryness and dissolving the residue in one litre of water. (*b*) A 10 per cent. solution of potassium cyanide. (*c*) A solution of sodium sulphide. Before making the test the lead solution is diluted to 100 volumes, so that each cubic centimetre contains 0·00001 grm. of lead. The solution to be tested is diluted to a definite volume. A measured portion of this solution is placed in a Nessler cylinder and 2 c.c. of the potassium cyanide solution are added, followed successively by sufficient ammonia to give an alkaline reaction and 2 c.c. of the sodium sulphide solution. A brown colour will be produced in the presence of lead. A second Nessler cylinder is taken. Some distilled water is poured in and then the potassium cyanide, ammonia and sodium sulphide as before. The diluted standard solution is now run in from a burette until the colour of the liquid

matches that of the first cylinder, the volumes of liquid in both being made the same by adding distilled water before finally matching. The object of adding potassium cyanide is to prevent copper or iron from contributing to the colour.

Zinc.

The principal zinc salts are **zinc sulphate,** $ZnSO_4 . 7 H_2O$, and **zinc chloride,** $ZnCl_2 . H_2O$. The zinc may be precipitated quantitatively from solutions of the salts either as zinc ammonium phosphate, zinc hydroxide or zinc sulphide.

Precipitation as Phosphate.—Treadwell's method is as follows (*Analytical Chemistry*, Vol. II., p. 140): If the solution is neutral, 2 to 3 grms. of ammonium chloride are added; if an acid solution is used ammonia is added until the solution is almost neutral (zinc ammonium phosphate dissolves in both acids and ammonia). The neutralised solution is diluted to 150 c.c., heated on the water-bath and ten times as much diammonium phosphate is added as there is zinc present. The diammonium phosphate should have an alkaline reaction to phenolphthalein; if it has not, sufficient dilute ammonia solution should be added to produce a pink colour. The precipitate, which is at first amorphous, becomes crystalline quickly if sufficient ammonium salts are present. After heating for 15 minutes, the precipitate is allowed to settle and filtered through a Gooch crucible, washed with a hot 1 per cent. solution of ammonium phosphate until free from chlorides, twice with cold water, then with 50 per cent. alcohol and dried at 110°–120° C. It may either be weighed as zinc ammonium phosphate, $ZnNH_4PO_4$, or ignited to pyrophosphate, $Zn_2P_2O_7$.

$$ZnNH_4PO_4 \times 0{\cdot}3664 = Zn.$$
$$Zn_2P_2O_7 \times 0{\cdot}4290 = Zn.$$

When *magnesium* or *aluminium* is present the method of Voigt is used: Excess of ammonia is added to the solution and then ammonium phosphate. The zinc ammonium phosphate is soluble in the excess of ammonia, and the precipitated ammonium phosphates of aluminium and magnesium are filtered off. If the filtrate be heated on the water-bath until the excess of ammonia is expelled, the zinc ammonium phosphate becomes insoluble.

Determination as Oxide.—The solution of the zinc salt should be free from ammonium salts and only slightly acid. Sodium carbonate is added a little at a time until a precipitate is just produced. The mixture is then boiled to complete the precipitation. A drop of phenolphthalein is added and then sodium carbonate solution drop by drop until a pink colour is produced. According to Treadwell (*loc. cit.*) if excess of sodium carbonate be added to the hot solution, some of it is adsorbed by the zinc carbonate and is difficult to wash out. The precipitate is filtered off on a Gooch crucible, washed, dried, ignited and weighed. ($ZnO \times 0{\cdot}8034 = Zn$.)

Determination as Sulphide.—When zinc sulphide is precipitated from an alkaline solution by means of ammonium sulphide it is very troublesome to filter, but if precipitated in the presence of formic, acetic or sulphocyanic acid it is thrown down in a granular condition and can be filtered readily. The solution is treated with a slight excess of ammonia and boiled, any precipitated iron or aluminium being filtered off. The filtrate is acidified with formic acid and saturated with sulphuretted hydrogen gas. The beaker is then heated on a water-bath for about 30 minutes and allowed to cool and stand for some time. The precipitated zinc sulphide is then filtered off on a Gooch crucible, washed, and ignited to zinc oxide, ZnO. When only small quantities of iron or aluminium

are present it is not necessary to remove them, since their sulphides are soluble in formic acid.

Both zinc chloride and zinc sulphate may be determined approximately from the specific gravities of their aqueous solutions.

Zinc Dust.—The value of zinc dust as a reducing agent is directly proportional to the percentage of metallic zinc which it contains, any other metallic impurities present being unable to act as reducing agents in alkaline solution.

Fraenkel's Method of analysis (*J.S.C.I.*, 1900, 931) is commonly used: About 1 grm. of the sample is weighed into a dry stoppered flask of about 200 c.c. capacity and treated with 100 c.c. of seminormal potassium bichromate solution and 10 c.c. of sulphuric acid (1 : 3). The flask is closed and shaken for 5 minutes and 10 c.c. more of the acid are then added and the mixture shaken again for 15 minutes. The zinc should now be completely dissolved. The solution is washed into a 500 c.c. flask, diluted to the mark, and 50 c.c. taken for titration. An excess of potassium iodide is added, the mixture diluted and the liberated iodine determined by titration with decinormal sodium thiosulphate solution in the usual manner. The test depends upon the reduction of the potassium bichromate by nascent hydrogen, 0·667 grm. of zinc reducing 1 grm. of the bichromate.

The use of *ferric salts*, such as ferric sulphate or iron alum, was suggested by Wahl (*J.S.C.I.*, 1897, 15): A weighed quantity of the sample is placed in a stoppered bottle with an excess of a neutral solution of ferric sulphate and the bottle is shaken for about 15 minutes. Sulphuric acid is then added, the solution diluted to a definite volume and a portion of it titrated with decinormal potassium permanganate solution to determine the ferrous iron produced in accordance with the equation

$$Fe_2(SO_4)_3 + Zn = ZnSO_4 + 2\ FeSO_4.$$

Wohl (*Ber.* 1904, **37,** 451) proposed to measure the *hydrogen* liberated from hydrochloric acid by a known quantity of the zinc. A stop-cock is fused to the neck of a flask of about 100 c.c. capacity. A weighed quantity of the zinc dust is introduced into the flask and the latter brought either to the temperature of the air or that of a water-jacket. The flask is then evacuated to an accurately determined pressure of about 60 mm. The tubulure of the stop-cock is then filled with water, and 5 c.c. of hydrochloric acid (sp. gr. 1·1) to which a drop of platinum chloride solution has been added are sucked into the flask. After the reaction is complete, the temperature is readjusted and the pressure measured. If the flask contained exactly 100 c.c., if the temperature is 20° C., and if 0·1788 grm. of zinc was weighed out, the percentage of metallic zinc is expressed by twice the difference of pressure in millimetres of mercury.

Magnesium.

The principal salts of magnesium are **magnesium chloride,** $MgCl_2 . 6\ H_2O$, and **magnesium sulphate** or Epsom salt, $MgSO_4 . 7\ H_2O$. The determination of magnesium has been described under Lime (p. 102).

Calcium.

Calcium Chloride, $CaCl_2$, crystallises with six molecules of water, but is generally bought in the anhydrous state either in the form of lumps or as granules. It is analysed in the following manner: A weighed quantity is dissolved in water. *Insoluble matter* is filtered off on a weighed Gooch crucible,

dried and weighed. The filtrate is diluted to a definite volume and the *calcium* determined in an aliquot part of the solution by precipitating as calcium oxalate and titrating the latter with decinormal potassium permanganate solution.

The Detection and Determination of Zinc and Magnesium in Size or Sized Goods.

The following method is due to Neale (*J.T.I.*, 1926, T 511): **Chlorides**: (*a*) In the case of cloth or yarn, 5 grms. of the sample are extracted with 20 c.c. of 2 *N* nitric acid and 300 c.c. of water in an open flask for one hour. The liquid is decanted off and filtered, 100 c.c. of water are added to the residue in the flask and the extraction repeated. The two filtrates are mixed and made up to 250 c.c. (Extract A). (*b*) For size, 1 grm. of the sample is heated overnight with 10 c.c. of 2 *N* nitric acid at about 90° C. and the almost clear liquid (filtered if necessary) is suitable for chloride determination (Extract B).

To determine chloride, 100 c.c. of extract A or the whole of extract B is treated with excess of decinormal silver nitrate solution, boiled, filtered and the precipitate washed. The filtrate and washings are titrated with decinormal thiocyanate solution.

Zinc and Magnesium: Cloth or yarn is extracted as described above (Extract A). For size, 1 grm. is evaporated to dryness several times with fuming nitric acid in a hard glass narrow-necked flask provided with a small funnel as a trap. The white residue is dissolved in hot dilute hydrochloric acid and the solution diluted to 100 c.c. (Extract C).

150 c.c. of extract A or the whole of extract C is treated with 20 c.c. of 2 *N* ammonium chloride solution, then made alkaline with ammonia and boiled. Any precipitate of ferric hydroxide is filtered off and the filtrate made just acid with hydrochloric acid. The solution is boiled, 20 c.c. of a 10 per cent. solution of diammonium hydrogen phosphate are added, followed by 15 c.c. of ammonium hydroxide (sp. gr. 0·880), and the mixture shaken for half an hour in a stoppered bottle, allowed to stand for some time and filtered. The white crystalline precipitate of magnesium ammonium phosphate, part of which adheres to the sides of the bottle, is washed three times with 2·5 per cent. ammonia solution. The filtrate and washings are boiled to remove ammonia, and cooled. Ten drops of a 0·4 per cent. solution of bromocresol purple are added and then dilute acetic acid until the purple colour changes to a greenish-grey. After standing for half an hour the zinc is precipitated from the neutral solution as zinc ammonium phosphate. This is soluble in both ammonia and acids. It is washed three times with small quantities of water. The washed precipitates of zinc and magnesium ammonium phosphates are now dissolved from the filters and the sides of the precipitation vessels with dilute nitric acid (15 c.c. of 25 per cent. nitric acid and 20 c.c. of water) and the filters washed. The solutions are treated with 25 c.c. of 34 per cent. ammonium nitrate solution, boiled, and 50 c.c. of a hot 3 per cent. solution of ammonium molybdate are run in from a tap funnel, with constant stirring. After standing for fifteen minutes, the yellow precipitate of ammonium phosphomolybdate is filtered off and washed with a cold 1 per cent. solution of sodium nitrate until the washings are neutral to litmus. The washed precipitate and filter paper are transferred to a beaker, treated with excess of normal sodium hydroxide solution and the unused alkali titrated with normal hydrochloric acid, phenolphthalein being used as indicator. There is no advantage in using more dilute reagents since the end-point is not sufficiently sharp. When precipitated under the foregoing conditions, one gramme-equivalent of alkali corresponds to 3·00 grms. of phosphorus pentoxide

(P_2O_5). From the quantity of phosphorus pentoxide found, the amount of zinc and magnesium can be calculated.

$$1{,}000 \text{ c.c. } N \text{ NaOH} \equiv 3{\cdot}00 \text{ grms. } P_2O_5.$$
$$\equiv 2{\cdot}77 \text{ grms. Zn } (5{\cdot}82 \text{ grms. } ZnCl_2).$$
$$\equiv 1{\cdot}03 \text{ grms. Mg } (4{\cdot}04 \text{ grms. } MgCl_2).$$

A delicate qualitative test for zinc is described by Cone and Cady (*Analyst*, 1927, 730). The filtrate containing the aluminium group of metals is acidified with hydrochloric acid, ammonium chloride added and the aluminium and iron hydroxides precipitated with ammonia. The filtrate from these is acidified with acetic acid. One part of it is tested for chromium and another part for zinc by the following test: 5 drops of a solution of 1 grm. of diphenylamine in 100 c.c. of glacial acetic acid are added, and also 5 c.c. of a 0·5 per cent. solution of potassium ferricyanide. The immediate appearance of a dark brown, green or purplish-black turbidity indicates the presence of zinc. The Cone and Cady test is useful for the identification of *zinc soaps* in fabrics. 1 grm. of diphenylamine is dissolved in 60 to 80 c.c. of 96 per cent. alcohol and the solution made up to 100 c.c. with 10 per cent. acetic acid. The sample is spotted with this reagent and then with a solution of potassium ferricyanide. In the presence of zinc a violet to black coloration is obtained.

Iron.

Iron forms divalent (ferrous) and trivalent (ferric) ions in solution, and apart from this it shows a great tendency to form *complex ions*, some of which are very stable. Every iron compound can be converted into the ferrous or ferric state by suitable reduction or oxidation processes, and the analysis depends upon the quantitative nature of these reactions. When in the ferrous state, iron can readily be determined with accuracy by titration with oxidising agents such as potassium permanganate. In the ferric state it can be precipitated in the form of ferric hydroxide, $Fe_2(OH)_6$, from solutions made slightly alkaline with caustic alkali.

The trivalent aluminium ion is only weakly basic in character. All of its salts have an acid reaction and are hydrolysed in hot or boiling solutions with the formation of insoluble basic compounds. The separation of iron from aluminium, which is a necessary procedure in the analysis of most aluminium compounds, is based upon the solubility of aluminium hydroxide in strong caustic alkalis and its insolubility in dilute ammoniacal solutions. It is to be noted, however, that the precipitation of aluminium hydroxide in ammoniacal solutions is retarded or inhibited by the presence of non-volatile organic acids or organic compounds containing hydroxyl groups.

Ferrous Sulphate.—Ferrous sulphate, $FeSO_4 . 7\,H_2O$, is produced by the oxidation of pyrites in open clay-lined pits. The product is lixiviated with water, the washings concentrated and boiled with scrap iron to reduce the dissolved ferric sulphate to the ferrous salt. The liquid is then concentrated further and the ferrous sulphate allowed to crystallise out. The crystals obtained in this manner are removed and boiled with sulphuric acid, then separated, drained, washed and dried. The product so obtained consists of bluish-green monoclinic crystals, whence the commercial terms "copperas" and "green vitriol." When exposed to moist air, the surface of the crystals becomes covered with a yellowish-brown film of a basic ferric sulphate.

In the textile industry ferrous sulphate is employed extensively as a mordant and as a reducing agent in the so-called "copperas vat." For these purposes

it should be free from copper, zinc and aluminium. The impurities generally associated with ordinary commercial ferrous sulphate are *free sulphuric acid* and *ferric salts*.

Insoluble Matter.—5 grms. of the salt are dissolved in water and the insoluble matter filtered off through a tared filter, washed, dried at 100°–105° C. and weighed. The insoluble residue may contain sparingly soluble *basic ferric sulphate*, which can be determined by dissolving in hydrochloric acid and precipitating as ferric hydroxide.

Determination of Ferrous Iron.—1 grm. of the sample is dissolved in about 100 c.c. of cold recently-boiled distilled water to which 50 c.c. of a 10 per cent. solution of sulphuric acid have been added. The acidified solution is then titrated with decinormal potassium permanganate solution until the pink coloration remains permanent for 30–60 seconds. 1 c.c. $N/10$ $KMnO_4 \equiv 0{\cdot}005584$ grm. $Fe \equiv 0{\cdot}0278$ grm. $FeSO_4 . 7 H_2O$.

Total Iron.—1–2 grms. of the sample are weighed into a flask fitted with a rubber bung through which passes a Bunsen valve. The salt is dissolved in water, and 5–10 c.c. of concentrated sulphuric acid and some pure zinc are added. The bung is then inserted and the flask placed on a water-bath until the ferric iron has been completely reduced. This is ascertained by removing a drop of the solution with a pointed glass rod and testing with ammonium thiocyanate solution. The solution is decanted into a 250 c.c. flask, the reaction flask and any residual zinc being washed with boiled distilled water, after which the solution is cooled, diluted to 250 c.c. and titrated with decinormal potassium permanganate. The difference between this result and the ferrous iron result is calculated to *ferric iron*. Naturally, if chemically-pure zinc is not obtainable, a weighed quantity must be used and allowed to dissolve completely, a blank experiment being carried out simultaneously.

Determination of Alumina (and Total Soluble Iron).—Instead of determining the total iron by titration with permanganate solution, or as a check on this method, the iron separated in the determination of alumina may be weighed. The filtrate from the determination of the insoluble matter is made up to 500 c.c. and 50 c.c. of it are boiled with nitric acid to oxidise the ferrous iron present. The liquid is then transferred to a porcelain dish, made strongly alkaline with pure sodium hydroxide solution, boiled, diluted with hot water and filtered. The precipitate which is formed consists of ferric hydroxide; the filtrate contains the alumina as sodium aluminate. The precipitate is washed with water, dissolved in hydrochloric acid, reprecipitated with ammonia, filtered off, dried, ignited, and weighed as Fe_2O_3. (1 grm. $Fe_2O_3 \equiv 0{\cdot}6994$ grm. Fe.). The filtrate from the ferric hydroxide is added to that obtained from the first precipitation, the mixture acidified with nitric acid, then made alkaline with ammonia and boiled. The aluminium hydroxide which is precipitated is filtered off, washed, dried, ignited and weighed as Al_2O_3. (1 grm. $Al_2O_3 \equiv 0{\cdot}5291$ grm. Al.)

Determination of Sulphuric and Hydrochloric Acids.—A weighed quantity of the salt is dissolved in water and the solution boiled with a little nitric acid to oxidise the iron. A slight excess of ammonia is then added and the mixture filtered. The filtrate and washings are cooled, made up to a definite volume and the hydrochloric and sulphuric acids determined in aliquot portions by the usual methods.

Ferric Sulphate is made by oxidising ferrous sulphate with nitric acid in the presence of sulphuric acid. It may consist of true ferric sulphate, $Fe_2(SO_4)_3$, or may contain *basic ferric sulphates* such as $Fe_2(SO_4)_2(OH)_2$, or *nitrato-sulphates* such as $Fe_2(SO_4)_2(NO_3)_2$. The analysis includes the determination of the total

iron, sulphuric and hydrochloric acids, and total acid. The *iron* is determined in the manner already described.

Determination of Total Acid.—2–5 grms. of the sample are dissolved in water, the solution filtered and the filtrate made up to 250 c.c. Portions of this solution are then treated with an excess of decinormal sodium carbonate solution and the liquid boiled and filtered. The residue is washed with boiling water and the washings added to the filtrate. On cooling, the excess sodium carbonate remaining in the filtrate is determined by titration with decinormal hydrochloric acid, using methyl orange as indicator. 1 c.c. $N/10$ $Na_2CO_3 \equiv 0{\cdot}004$ grm. SO_3.

Determination of Sulphuric and Hydrochloric Acids.—The determination of the sulphuric acid content of samples of ferric sulphates and nitrato-sulphates is best carried out by precipitating the iron with ammonia from a boiling solution of the sample which has been acidified with nitric acid and boiling off the excess. The filtrate from this precipitate is cooled, made up to 250 c.c. in a graduated flask and aliquot portions of the solution taken for the determination of the sulphuric and hydrochloric acids.

To determine the hydrochloric acid, 100 c.c. of the solution are pipetted into a beaker and 5 c.c. of nitric acid added. An excess of a solution of silver nitrate is then added and the solution boiled to coagulate the precipitated silver chloride, which is then filtered off, dried and weighed.

The sulphuric acid present is determined in a fresh 100 c.c. portion of the solution by acidifying with hydrochloric acid and precipitating the sulphates present with barium chloride solution, as described in the analysis of hydrochloric acid.

Basicity of Ferric Sulphate.—In valuing ferric sulphates the *ratio* of the *total acid* to *ferric oxide* is of primary importance since, for most purposes the salt should contain less acid than that corresponding to the normal sulphate. The amount of SO_3 required to combine with the determined quantities of ferrous and ferric oxides to form the normal sulphates is calculated and compared with the actual SO_3 content of the sample.

Determination of Nitric Acid.—The nitric acid content of nitrato-sulphates may be taken as the difference between the total acid content and the sum of the hydrochloric and sulphuric acids found.

Ferrous Acetate $(CH_3COO)_2Fe$.—The commercial solution of ferrous acetate known as "pyrolignite of iron," "iron liquor" or "black liquor," is made by treating scrap iron with acetic acid, and also by decomposing ferrous sulphate with calcium acetate and filtering off the precipitated calcium sulphate. When made by the latter method the solution will always contain *calcium*. Before determining iron, the solution should be evaporated to dryness, and the residue ignited gently to destroy organic matter. The residue is then dissolved in hydrochloric acid, the solution filtered and made up to a definite volume. The *iron* is determined by reducing a portion of the solution with zinc and titrating with decinormal potassium permanganate solution. The *acetic acid* may be determined in a separate portion of the sample by acidifying it with sulphuric acid, distilling and titrating the distillate with decinormal sodium hydroxide in the presence of phenolphthalein.

Potassium Ferrocyanide, $K_4Fe(CN)_6 \cdot 3\,H_2O$.—When potassium ferrocyanide is oxidised in an acid solution the ferricyanide is formed:

$$K_4Fe(CN)_6 + 2\,H_2SO_4 = 2\,K_2SO_4 + H_4Fe(CN)_6,$$
$$2\,H_4Fe(CN)_6 + O = 2\,H_3Fe(CN)_6 + H_2O.$$

The salt is dissolved in water, the solution acidified with sulphuric acid and decinormal potassium permanganate run in until a faint pink colour is produced. The end-point is difficult to see unless the solution is very dilute. The titration should be carried out in a large porcelain dish, the liquid under titration being diluted to about 500 c.c. The pink colour can then be observed at the edge of the liquid in the dish.

$$1 \text{ c.c. } N/10\ KMnO_4 \text{ solution} \equiv 0{\cdot}0368 \text{ grm. } K_4Fe(CN)_6 \text{ or } 0{\cdot}04224\ K_4Fe(CN)_6 \,.\, 3\,H_2O.$$

The *iron* and *potassium* can be determined in the solution obtained by boiling the ferrocyanide with sulphuric acid (in a draught chamber).

Colorimetric Determination of Iron.—A standard solution of iron is prepared by dissolving one gramme of pure iron wire in hydrochloric acid. The solution is evaporated to dryness on the water-bath with a little nitric acid to oxidise the iron. More hydrochloric acid is then added and the solution again evaporated to dryness. The residue is dissolved in a little dilute hydrochloric acid and the solution diluted to one litre (1 c.c. ≡ 0·001 grm. Fe). Before use the solution is diluted until each cubic centimetre contains 0·00001 grm. of iron. The liquid to be tested is acidified with hydrochloric acid, a little bromine water added to oxidise any ferrous iron present and the excess of bromine boiled off. It is then poured into a Nessler cylinder and 2 c.c. of a freshly prepared one per cent. solution of potassium ferrocyanide are added. Distilled water and the same volume of potassium ferrocyanide solution are placed in a second cylinder and the diluted standard iron solution is run in until the colour of the two liquids is the same. It must be remembered that Prussian blue is decomposed by alkalis, but not by cold hydrochloric or sulphuric acid.

Aluminium.

The compounds of aluminium used in connection with textile processes are

Aluminium sulphate,	$Al_2(SO_4)_3 \,.\, 18\,H_2O$.
Ammonium alum,	$Al_2(SO_4)_3 \,.\, (NH_4)_2SO_4 \,.\, 24\,H_2O$.
Potash Alum,	$Al_2(SO_4)_3 \,.\, K_2SO_4 \,.\, 24\,H_2O$.
Aluminium chloride,	Al_2Cl_6.
Aluminium acetate,	$(CH_3COO)_6Al_2$.
Aluminium thiocyanate,	$Al_2(CNS)_6$.

Sulphato-acetates, such as $(CH_3COO)_4Al_2SO_4$, are used also but are prepared as required by treating a solution of aluminium sulphate with a suitable quantity of lead acetate. Basic aluminium salts are obtained by treating solutions of aluminium sulphate or other aluminium salt with an alkali, such as sodium carbonate, thus :

$$2\,Al_2(SO_4)_3 + 2\,Na_2CO_3 + 2\,H_2O = 4\,Al(SO_4)OH + 2\,Na_2SO_4 + 2\,CO_2.$$
$$2\,Al_2(SO_4)_3 + 3\,Na_2CO_3 + 3\,H_2O = Al_4(SO_4)_3(OH)_6 + 3\,Na_2SO_4 + 3\,CO_2.$$
$$2\,Al_2(SO_4)_3 + 4\,Na_2CO_3 + 4\,H_2O = 2\,Al_2(SO_4)(OH)_4 + 4\,Na_2SO_4 + 4\,CO_2.$$

Aluminium Sulphate.—*Aluminium* is determined by precipitation with ammonium hydroxide, filtering off the aluminium hydroxide and weighing as alumina, Al_2O_3. Aluminium sulphate, $Al_2(SO_4)_3 \,.\, 18\,H_2O$, contains 15·33 per cent. of alumina, or 51·37 per cent. of $Al_2(SO_4)_3$.

Iron, if present, may be separated by dissolving the aluminium hydroxide in pure sodium hydroxide, diluting the mixture and filtering off the undissolved iron oxide. It may also be determined directly by titration with decinormal potassium permanganate after reduction with zinc, or if only traces are present, by a colorimetric method.

White's Method for the Determination of Aluminium and Basicity (*J.S.C.I.*, 1902, 793).—50 c.c. of the aluminium solution are pipetted into a titrating flask, 100 c.c. of a 10 per cent. solution of neutral potassium sodium tartrate added, and the liquid titrated with decinormal barium hydroxide solution, using phenolphthalein as indicator. Another 50-c.c. portion of the solution is evaporated to dryness on a water-bath and the residue dissolved in 100 c.c. of a 10 per cent. solution of sodium citrate; the liquid is then allowed to stand for 10 minutes and titrated with decinormal barium hydroxide solution as before.

In the presence of neutral potassium sodium tartrate, and using phenolphthalein as indicator, the quantity of barium hydroxide solution required corresponds to the sulphuric acid anhydride combined with the alumina as aluminium sulphate, $Al_2O_3 \cdot 3\,SO_3$, plus the free sulphuric acid anhydride (that combined as potassium or ammonium sulphate does not affect the result). On the other hand, if the tartrate is replaced by sodium citrate, the barium hydroxide required corresponds to the whole of the free sulphuric acid anhydride plus two-thirds of that combined with the alumina. Consequently, if V_1 is the volume of barium hydroxide solution used in the first titration and V_2 is the volume used in the second titration, then

$$3\,(V_1 - V_2) \times 0{\cdot}0034 = \text{grms. } Al_2O_3.$$
$$V_1 - 3\,(V_1 - V_2) \times 0{\cdot}004 = \text{grms. free } SO_3.$$

In these titrations the precipitation of barium sulphate does not take place for several hours.

Aluminium Acetate.—The normal salt, $(CH_3COO)_6Al_2$, is not known in the pure state. The product used in the textile industries, "red liquor," is prepared by the action of aluminium sulphate on crude calcium acetate.

Determination of Aluminium.—A weighed portion of the sample is ignited until the organic matter is completely destroyed and the aluminium determined by the methods already given.

Determination of Acetic Acid.—The determination of the acetic acid is best effected by distilling a quantity of a solution of the sample with phosphoric acid. The distillate is collected and titrated with decinormal sodium hydroxide solution, using phenolphthalein as indicator. About 25 c.c. of an approximately normal solution of the sample are diluted to 150 c.c. with water and about 10 c.c. of syrupy phosphoric acid added. The mixture is distilled until about 100 c.c. have been collected. 100 c.c. of water are then added to the residual liquor in the flask and the distillation continued until exactly 200 c.c. of distillate have been collected. Aliquot portions of the distillate are titrated with the standard alkali. 1 c.c. $N/10$ NaOH $\equiv$ 0·0060 grm. CH_3COOH.

Aluminium Sulphato-acetate.—The aluminium sulphato-acetates are prepared in a similar manner to the iron nitrato-sulphates, by treating a solution of aluminium sulphate with a smaller quantity of lead acetate than that required for the production of the normal salt. In the analysis of these compounds the organic matter is first destroyed, the *iron* and *alumina* are then separated and determined, and the *sulphuric anhydride* precipitated by means of barium chloride solution.

Copper.

The only salt of copper which is used to any extent in dyeing is copper sulphate ("blue stone" or "blue vitriol"), $CuSO_4 . 5 H_2O$. The chief impurity in it is *ferrous sulphate* or *ferric sulphate*. When the former is present it is precipitated gradually from an aqueous solution as a *basic ferric sulphate*.

Copper Sulphate.—An aqueous solution is prepared, *insoluble matter* being filtered off on a Gooch crucible and weighed. *Iron* is determined in a portion of the filtrate after precipitating the copper with sulphuretted hydrogen in the presence of hydrochloric acid and filtering off the copper sulphide. The filtrate is boiled with nitric acid until the sulphuretted hydrogen has been removed. It is then filtered to remove sulphur, excess of ammonia added and the liquid boiled, after which the ferric hydroxide is filtered off, ignited and weighed.

Copper may be determined by either a gravimetric or a volumetric method. In the absence of other metals whose hydroxides are insoluble the copper can be precipitated as hydroxide and weighed as *oxide*. When other metals such as iron are present, the solution is acidified with hydrochloric acid and treated with sulphuretted hydrogen. The precipitated copper sulphide is filtered off, washed with sulphuretted hydrogen water and dissolved in a little nitric acid. The solution is boiled until free from sulphuretted hydrogen and any undissolved sulphur filtered off. It is then diluted to about 250 c.c., brought to the boiling-point, and whilst boiling a solution of sodium hydroxide added little by little until the reaction of the liquid becomes just alkaline. The precipitate should consist of granular black copper oxide; if flocculent, boiling should be continued. The precipitate is allowed to settle and the clear liquid decanted through a weighed Gooch crucible. The precipitate is washed by decantation with hot water and finally transferred to the Gooch, dried, ignited and weighed.

$$CuO \times 0{\cdot}7989 = Cu.$$
$$CuO \times 3{\cdot}137 = CuSO_4 . 5 H_2O.$$

Great care must be taken to avoid a large excess of alkali, since this is very difficult to remove by washing.

An accurate method for the determination of copper depends upon the insolubility of *cuprous thiocyanate*, $Cu_2(CNS)_2$. The copper solution is made slightly acid with hydrochloric or sulphuric acid and saturated with sulphur dioxide. A cold aqueous solution of ammonium thiocyanate is then added, drop by drop and with constant stirring, until a white precipitate consisting of cuprous thiocyanate separates. After standing for some hours this precipitate is filtered off on a weighed Gooch crucible and washed with cold water until the washings give only a faint reaction with ferric chloride. The precipitate is then washed several times with 20 per cent. alcohol, dried at 110° to 120° C. and weighed. Jamieson, Levy and Wells (*J.S.C.I.*, 1908, 572) described a *volumetric* modification of this process. The washed cuprous thiocyanate is placed in a 250 c.c. stoppered bottle, together with 5 c.c. of chloroform and 30 c.c. of concentrated hydrochloric acid, and titrated with a standard solution of potassium iodate, the stopper being replaced and the bottle shaken after each addition of the iodate solution. The violet colour of the chloroform solution disappears with great sharpness at the end of the titration. If the solution of potassium iodate contains 5·05 grms. of KIO_3 per litre, each cubic centimetre is equivalent to 0·001 grm. of copper.

The equations are:

(*a*) $2CuSCN + 3KIO_3 + 4HCl = 2CuSO_4 + I_2 + ICl + 2HCN + 3KCl + H_2O.$
(*b*) $2I_2 + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O.$

Copper may be determined *volumetrically* by adding an excess of potassium iodide solution to its aqueous or slightly acid solution and titrating the liberated iodine with sodium thiosulphate solution. The copper is precipitated as cuprous iodide in accordance with the equation

$$2\,CuSO_4 + 4\,KI = Cu_2I_2 + 2\,K_2SO_4 + I_2.$$

Very small quantities of copper, such as may occur in fabrics, can be estimated by a *colorimetric* process. The copper is separated from the solution or extract of the ash as sulphide. This is dissolved in nitric acid and the solution evaporated to dryness. The residue is dissolved in water and made up to a definite volume. A portion of this solution is placed in a Nessler cylinder, a little ammonium acetate solution added and then a few drops of a dilute solution of potassium ferrocyanide. A reddish colour due to copper ferrocyanide is produced, which is matched with that given by a solution of copper sulphate containing 0·00001 grm. of copper per cubic centimetre. The addition of ammonium acetate is necessary to remove any traces of nitric acid which may be present.

Callan and Henderson (*Analyst*, 1929, 650) found that *sodium diethyl-dithiocarbamate*, $C{\leqq}\begin{matrix}N(C_2H_5)_2\\ S\\ SNa\end{matrix}$, is an extremely delicate reagent for the detection and determination of copper when used in a 0·1 per cent. aqueous solution. The solution to be tested, after removing other metals when necessary, is made up to 100 c.c. with distilled water. An aliquot part is run into a Nessler cylinder, diluted with water, made slightly alkaline with ammonia, and 10 c.c. of the reagent added, the mixture being diluted to 100 c.c. A golden-brown colour is produced when the solution contains one part of copper per million. *Quantitative* determinations may be made by matching with the colour produced by suitable volumes of a solution containing 0·00001 grm. of copper per cubic centimetre, but not more than 0·0001 grm. of copper in 100 c.c. should be present. Iron, lead and zinc interfere with the reaction, but may be removed in the following manner: (*a*) Excess of ammonia is added and the solution filtered; this removes iron. (*b*) The solution is treated with a few drops of 10 per cent. ferric chloride solution, made alkaline with ammonia and boiled. The lead is removed with the precipitate and the whole of the copper is found in the filtrate. (*c*) When the zinc does not exceed 0·1 grm. per 100 c.c. (*i.e.* 1000 times the maximum amount of copper for which the test is applicable), the addition of 0·880 sp. gr. ammonia (2 to 5 c.c. per 100 c.c.) prevents interference, provided that the volume of the reagent recommended is not largely exceeded.

Some other sensitive tests for copper may be mentioned, since they are useful in the detection of *cuprammonium silk*:

(1) 5 grms. of the sample are burnt to an ash. The ash is dissolved in hydrochloric acid, the solution made alkaline with ammonia and filtered. The filtrate is concentrated to 5 c.c. and tested as follows: One drop of *potassium ethyl xanthate* gives a yellow colour; *potassium ferrocyanide* gives a pink colour; and concentrated *hydrobromic acid* (free from bromine) a red precipitate of the composition $CuBr_2 . HBr . 2\,H_2O$.

(2) The solution, which must be free from chlorides, is neutralised and then made faintly acid by adding one drop in excess of 1 in 3 sulphuric acid. It is then placed in a 100 c.c. Nessler cylinder, made up to volume, 1 grm. of ammonium persulphate is dissolved in the solution, 1 c.c. of saturated alcoholic *dimethylglyoxime*, 0·5 c.c. of a 0·5 per

cent. solution of silver nitrate and 2 c.c. of 10 per cent. aqueous pyridine added, and the whole stirred. If one part in 10,000,000 of copper be present, a reddish-violet colour resembling that of permanganate is produced. (Clarke and Jones, *Analyst*, 1929, 333).

Chromium.

The compounds of chromium used in the textile industry are

Potassium bichromate,	$K_2Cr_2O_7$.
Sodium bichromate,	$Na_2Cr_2O_7 . 2 H_2O$.
Chrome alum,	$K_2SO_4 . Cr_2(SO_4)_3 . 24 H_2O$.
Chromium fluoride,	$CrF_3 . 4 H_2O$.

Bichromates.—Potassium bichromate is a comparatively pure substance even in the commercial form. The sodium salt is, however, deliquescent and may contain *chromic oxide, normal sodium chromate* and *sodium sulphate.*

An approximately decinormal solution of the bichromate is made up, and any *insoluble matter* filtered off, weighed and examined. In the case of sodium bichromate the insoluble matter sometimes contains chromium sesquioxide.

The following determinations are made on the filtered solution :

(1) Total chromium.
(2) Chromium as bichromate.
(3) ,, ,, chromate.
(4) ,, ,, free chromic acid.
(5) Sulphates.

Determination of Total Chromium.—The total chromium may be determined by either a *gravimetric* or a volumetric method. The former is only applicable in the absence of iron and aluminium. A measured volume of the solution is acidified, a little sodium sulphite added and the liquid boiled until the sulphur dioxide has been expelled. The solution is then made alkaline with ammonia, and after boiling, the chromium hydroxide is filtered off, washed and ignited to Cr_2O_3. 1 grm. $Cr_2O_3 \equiv 0{\cdot}6844$ grm. Cr.

In the *volumetric* method a portion of the solution is treated with a little sodium peroxide and the mixture boiled until the hydrogen peroxide has been decomposed. The solution is cooled, acidified with hydrochloric acid and treated with potassium iodide, after which the iodine liberated is titrated with decinormal sodium thiosulphate solution, starch being added towards the end of the titration as an indicator. Chromium salts, if present, are converted by sodium peroxide into sodium chromate :

$$2\,Cr(OH)_3 + 4\,NaOH + 3\,O = 2\,Na_2CrO_4 + 5\,H_2O.$$

Both chromates and bichromates liberate iodine from potassium iodide, the former being first changed into bichromate by the action of the acid :

$$2\,Na_2CrO_4 + 4\,HCl = H_2Cr_2O_7 + 4\,NaCl + H_2O,$$
$$H_2Cr_2O_7 + 6\,KI + 12\,HCl = 2\,CrCl_3 + 6\,KCl + 7\,H_2O + 3\,I_2.$$

When *iron* is present it will be precipitated by the sodium peroxide as ferric hydroxide and may be filtered off and weighed. *Aluminium* on the other hand remains in solution.

1 c.c. $N/10$ sodium thiosulphate $\equiv 0{\cdot}00173$ grm. Cr,
,, ,, $= 0{\cdot}00253$ grm. Cr_2O_3,
,, ,, $= 0{\cdot}0147$ grm. $K_2Cr_2O_7$.

The chief difficulty in the method is that it is necessary to boil the liquid for about half an hour to ensure the expulsion of the hydrogen peroxide. If any be left it will decompose potassium iodide and hence make the result too high. The addition of a little manganese dioxide or potassium permanganate causes the rapid decomposition of the peroxide:

$$MnO_2 + H_2O_2 = MnO + H_2O + O_2,$$
$$MnO + 2\,HCl = MnCl_2 + H_2O.$$

A convenient way of determining the total chromium consists in mixing a weighed quantity of the finely powdered bichromate with about five times its volume of a mixture of equal parts of magnesia and anhydrous sodium carbonate and heating the mixture in a platinum or silica dish, stirring it occasionally with a platinum wire. The mixture is then washed into a flask, acidified with hydrochloric acid and titrated as before.

Determination of Normal Chromate and Chromic Acid.—Sodium chromate is neutral towards phenolphthalein, but both bichromates and chromic acid are acid towards this indicator. Hence, sodium bichromate may be determined by titration with decinormal sodium hydroxide in the presence of phenolphthalein, the end-point indicating the completion of the reaction:

$$Na_2Cr_2O_7 + 2\,NaOH = 2\,Na_2CrO_4 + H_2O,$$
$$H_2CrO_4 + 2\,NaOH = Na_2CrO_4 + 2\,H_2O.$$

The difference between the total chromium already found and that given by this titration may be calculated to *sodium chromate*.

$$1 \text{ c.c. } N/10\ NaOH \equiv 0{\cdot}0147 \text{ grm. } K_2Cr_2O_7\ (0{\cdot}01 \text{ grm. } CrO_3) \text{ or } 0{\cdot}005 \text{ grm. of free } CrO_3.$$

Free *chromic acid* requires twice as much sodium hydroxide as it would if the chromium were present as bichromate, whilst if present as chromate it would react with none. Procter gives the following rule: "If the decinormal soda required to neutralise is less than one-third of the decinormal thiosulphate required for the chromium, each c.c. used corresponds to 0·010 grm. of chromic acid as bichromate or 0·0147 grm. of potassium bichromate, and the remainder of the chromic acid indicated by the thiosulphate will be present as neutral chromate. If the soda is more than one-third of the thiosulphate solution, each c.c. in excess of one-third corresponds to 0·005 grm. of free CrO_3 and the remainder indicated by the thiosulphate is bichromate. If the soda exceeds two-thirds of the thiosulphate, the whole of the chromic acid is free and the excess of soda over two-thirds is due to some other acid."

Free chromic acid may be determined also by the process of Procter and Heal (*J.S.C.I.*, 1895, 248), which depends upon the fact that hydrogen peroxide oxidises chromic acid to perchromic acid, which dissolves in ether with the formation of a blue solution. A measured volume of the solution is placed in a small separating funnel, and 2 c.c. of neutral hydrogen peroxide and 20 c.c. of ether are added. Sufficient decinormal sodium carbonate solution is then added to make the solution slightly alkaline, and the liquid then titrated with decinormal hydrochloric acid, shaking the mixture after each addition, until the ether acquires a faint blue tinge. If the volume of acid used be deducted from the volume of sodium carbonate solution added, the difference is the sodium carbonate used in converting the free chromic acid into chromate; each c.c. corresponds to 0·005 grm. of chromic acid (CrO_3).

Chromium Present as Chromate or Bichromate.—This is determined by direct titration. A portion of the chromium solution is treated with potassium iodide and acidified with hydrochloric acid, after which the liberated iodine is titrated with decinormal sodium thiosulphate solution. A *gravimetric* method may be used also if desired: The chromium solution is made faintly alkaline and then slightly acid with acetic acid. It is then boiled and a solution of barium acetate added, drop by drop, to the boiling liquid, until no more precipitate is formed. After standing for some time the barium chromate is filtered off on a Gooch crucible, washed with dilute alcohol and dried. The crucible is then covered and suspended in a larger crucible by means of an asbestos ring and heated, at first gently for a short time and finally strongly for five minutes. The lid is then removed and the heating continued until the chromate has a uniform yellow colour. 1 grm. $BaCrO_4 \equiv 0{\cdot}2052$ grm. Cr.

Determination of Sulphates.—100 c.c. of the solution of the sample are boiled with 5 c.c. of concentrated hydrochloric acid and a further 2–3 c.c. of acid are added to the boiling liquid, followed immediately by a sufficient quantity of a boiling solution of barium chloride to precipitate the whole of the sulphates present. The precipitate is allowed to settle, the supernatant liquid decanted through a tared Gooch crucible and the residue washed several times with distilled water containing a little hydrochloric acid and finally with boiling water. The residue is then transferred to the filter, again washed with boiling water, dried, ignited, and weighed. 1 grm. $BaSO_4 \equiv 0{\cdot}4115$ grm. SO_4.

Chromium Salts.—The chromium is determined by one of the methods already described. The volumetric process is the most suitable, since it separates iron simultaneously. The acid may be determined and other acids detected in the usual manner.

Commercial *chrome alum* may contain *calcium sulphate* as an impurity. Calcium would be determined in the filtrate after precipitating the chromium by means of ammonia.

Determination of the Basicity of a solution of chromium salts. The basicity of a solution of chromium sulphate may be expressed in two ways, viz.:

(1) In terms of grammes of SO_4 combined with 52 grammes of chromium.
(2) By the method of the Society of Leather Trades Chemists (*J.L.T.C.*, 1924, 505), which defines basicity as

$$\frac{\text{chromium combined with hydroxyl} \times 100}{\text{total chromium}}.$$

The determination is carried out in the following manner: A measured volume of the solution, which should contain 0·2–0·3 grm. of chromium, is run into a porcelain dish and diluted to 400 c.c. with distilled water; 3–4 c.c. of a one per cent. solution of phenolphthalein are added and the mixture titrated with decinormal sodium hydroxide solution until a pink colour is produced. The liquid must be stirred continuously during the titration. When the pink colour appears the contents of the basin are boiled and the titration continued. The end-point is the production of a greyish-violet tint in the stirred liquid or a pink colour when viewed against the side of the basin after allowing the precipitate to settle. When near the end-point the boiling is discontinued. Each cubic centimetre of $N/10$ sodium hydroxide used is equivalent to 0·0048 grm. of SO_4 combined with trivalent chromium. The total chromium is determined by titration and that combined with hydroxyl obtained by difference.

The basicity of $Cr_2(SO_4)_3$ is 0, that of $Cr(OH)_3$ 100, and that of $Cr(OH)SO_4$ 33·33. By multiplying the basicity by 0·06 the number of hydroxyl groups in

combination with chromium (Cr_2) is obtained. Thus $33{\cdot}33 \times 0{\cdot}06 = 2$ and the formula of a basic salt of basicity 33·33 is $Cr_2(OH)_2(SO_4)_2$ or $Cr(OH)SO_4$.

If it is desired to express the basicity in terms of SO_4 combined with chromium, the titration is carried out in the manner described, and the basicity is given by $Cr : SO_4 = 52 : x$. The relation between the two methods of expression is shown by the following formulae, where X is the old and B the new method :

$$\frac{144 - X}{144} \times 100 = B,$$

$$\frac{100 - B}{100} \times 144 = X.$$

The Determination of Fluorine in Chromium Fluoride.—The solution is boiled with a slight excess of sodium carbonate solution and filtered. The filtrate and washings are brought to the boiling-point and the fluorine precipitated as *calcium fluoride* by adding a solution of calcium acetate to the boiling mixture. The precipitate is filtered off, washed, dried, and ignited in a platinum crucible. After ignition it is treated with excess of dilute acetic acid to dissolve the lime and the mixture evaporated to dryness on a water-bath. The residue is treated with a few drops of dilute acetic acid and the calcium fluoride filtered off, washed, dried and ignited. The result may be checked by decomposing the fluoride carefully with sulphuric acid, driving off the excess acid, igniting the residue and weighing the calcium sulphate. According to Treadwell (*Analytical Chemistry*, Vol. II, 1919, p. 471), unless a slight excess of sodium carbonate is present in the first precipitation, the calcium fluoride is very difficult to filter.

Tin.

Tin occurs in combination in two forms, viz. divalent and tetravalent tin. The former, or stannous compounds, act as powerful reducing agents and are comparatively easily oxidised to stannic salts even under ordinary atmospheric conditions. Tin compounds employed in the textile industries are known by a large number of synonyms. Thus :

(*a*) *Stannous chloride* or " tin crystals," " tin salt," " single muriate of tin," " double muriate of tin," etc.

(*b*) *Mixtures of stannous salts* of indefinite composition, such as " yellow spirit," " amaranth " and " plum spirit," " scarlet finishing spirit " or " finishing spirit."

(*c*) *Stannous nitrate* or " bowl spirit," " scarlet spirit," " nitrate of tin."

(*d*) *Stannic ammonium chloride* (now rarely used) or " pink crystals."

(*e*) *Stannic chloride* and *mixtures of stannic compounds* of indefinite nature, such as " tin spirits," " nitro-muriate of tin," " tin composition," " cotton spirits," " barwood spirits," " crimson spirits," " purple spirits," " physic," " symuriate of tin," " pink cutting liquor," etc.

(*f*) *Sodium stannate*, referred to as " preparing salt."

The determination of the tin content of these materials is performed in the manner described for stannous and stannic chlorides. A careful qualitative examination of the samples must be made in order to determine the other acids present, and their amounts determined by the methods described under the various acids.

The chief reactions employed for the detection of stannous and stannic ions are the following:

(*a*) *Stannous Compounds.*—Hydrogen sulphide precipitates the brown hydrated sulphide from solutions of stannous salts. The precipitate is soluble in alkalis but is reprecipitated on acidifying. Mercuric chloride gives a white precipitate of mercurous chloride. If an excess of the stannous chloride is added the precipitate is reduced to metallic mercury. Ferric chloride, when added to a solution of potassium ferricyanide, produces a darkening in the colour of the solution; then on addition of an aqueous solution of a stannous compound a blue precipitate of ferrous ferricyanide is formed.

(*b*) *Stannic Compounds.*—Hydrogen sulphide yields a yellow precipitate of stannic sulphide. In the presence of a small amount of hydrochloric acid this precipitation is quantitative. The precipitate is soluble in ammonium sulphide and caustic alkalis, boiling hydrochloric acid and aqua regia. It is insoluble in ammonia and ammonium carbonate, while concentrated nitric acid converts it into metastannic acid. Sodium sulphate and sulphuric acid also yield a precipitate with stannic salts.

Analysis of Commercial Stannic Chloride.—Stannic chloride, $SnCl_4$, is prepared by dissolving metallic tin in hydrochloric acid and subsequent oxidation of the stannous chloride by potassium chlorate or nitrate. It is also prepared from tin plate cuttings by stripping them with chlorine. Stannic chloride from the latter source may contain *stannic oxychloride* and *metastannic acid*. For textile purposes, other impurities which should be absent are *free acid*, *stannous* and *iron compounds*. Samples of stannic chloride should be examined by qualitative tests for these latter substances.

Stannic chloride is a fuming liquid with a boiling-point of 114° C. When treated with small quantities of water it forms crystals of the composition $SnCl_4 . 3\,H_2O$, known as "butter of tin," but other hydrates $SnCl_4 . 5\,H_2O$ and $SnCl_4 . 8\,H_2O$ are known also. When dissolved in a large quantity of water it undergoes hydrolysis with the formation of orthostannic acid, $Sn(OH)_4$:

$$SnCl_4 + 4\,H_2O = 4\,HCl + Sn(OH)_4.$$

When orthostannic acid is boiled with water it is converted into insoluble metastannic acid which, when dried, yields tin dioxide:

$$\begin{aligned} Sn(OH)_4 &= H_2O + H_2SnO_3, \\ H_2SnO_3 &= H_2O + SnO_2. \end{aligned}$$

Commercial stannic chloride may consist either of the solid salt, $SnCl_4 . 5\,H_2O$, or of a concentrated aqueous solution.

The quantitative determination of the components may be carried out either by gravimetric or volumetric methods, but the latter are strictly applicable only when no free hydrochloric acid is present.

In view of the hygroscopic nature of the crystalline salt and its concentrated solutions, the weighings should be conducted in a stoppered weighing bottle.

Qualitative Analysis.—Stannic chloride should be free from the following impurities: Iron, stannous chloride, nitric acid or nitrates, sulphuric acid. *Iron* is detected by means of potassium sulphocyanide, and *stannous chloride* by the formation of a precipitate of mercurous chloride with mercuric chloride. *Sulphuric acid* is identified by the formation of a precipitate with barium chloride, and *nitric acid* by the brown ring test with ferrous sulphate.

Quantitative Analysis.—Specific Gravity.—The table over page shows the

relation between the specific gravity and the content of stannic chloride for aqueous solutions of pure stannic chloride (Heermann, *J.S.C.I.*, 1907, 819).

°Bé.	Tin, per cent.	°Bé.	Tin, per cent.	°Bé.	Tin, per cent.	°Bé.	Tin, per cent.
65·7	29·45	58·0	25·84	50·0	22·20	32·0	14·00
65·0	29·12	57·0	25·38	49·0	21·74	31·0	13·56
64·0	28·64	56·0	24·93	48·0	21·29	30·0	13·11
63·0	28·17	55·0	24·47	47·0	20·83	29·0	12·67
62·0	27·70	54·0	24·02	46·0	20·38	28·0	12·23
61·0	27·24	53·0	23·56	...	...	27·0	11·79
60·0	26·77	52·0	23·11	34·0	14·90	26·0	11·35
59·0	26·30	51·0	22·65	33·0	14·15	25·0	10·91

Determination of Tin.—About 1 grm. of the solid salt or twice as much of the liquid preparation is weighed out in a stoppered weighing bottle, washed into a beaker, the liquid diluted to about 300 c.c. with water and neutralised to methyl orange with a dilute solution of ammonia. Care must be taken not to make the solution strongly alkaline, since stannic hydroxide is soluble in ammonia. The tin is then precipitated by adding ammonium nitrate and boiling the mixture for a short time. The precipitate is filtered off on a weighed Gooch crucible, washed with a dilute solution of ammonium nitrate, dried, ignited, and weighed as tin oxide, SnO_2. It should be noted that when antimony is present Sb_2O_5 will be precipitated with the tin, and the method cannot then be used.

Determination of Chloride.—The filtrate and washings from the foregoing are acidified with nitric acid, excess of silver nitrate solution is added and the mixture boiled to coagulate the silver chloride. This is then filtered off on a Gooch crucible, washed with water acidified with nitric acid, dried at 130° C. and weighed.

If less chlorine is found than that corresponding to the amount in combination with the tin as $SnCl_4$, the presence of some other acid in an amount proportionate to the difference is indicated, or stannous chloride may be present.

Treadwell (*Analytical Chemistry*, Vol. II, p. 574) gives the following volumetric method of analysis: A weighed quantity of the sample is diluted with water and the *hydrochloric acid* liberated by hydrolysis is determined by titration with decinormal sodium hydroxide solution in the presence of methyl orange. The *total chlorine* is then determined by adding a few drops of neutral potassium chromate solution and titrating with decinormal silver nitrate solution. If more chlorine is found than corresponds with the acid neutralised in the first titration, the difference is expressed in terms of potassium chloride (potassium chlorate or nitrate is used sometimes in the preparation of stannic chloride). On the other hand, if less chlorine is found than corresponds to the acid neutralised, the presence of some acid other than hydrochloric acid is indicated.

Stannous chloride is determined by titration with iodine or potassium permanganate, as described under Stannous Chloride.

Stannous Chloride, $SnCl_2 . 2\,H_2O$, is made by dissolving the metal in concentrated hydrochloric acid and concentrating the solution. It forms colourless crystals which are readily soluble in water, but when damp or dissolved in water it is hydrolysed to a certain extent with the formation of an insoluble basic salt, Sn(OH)Cl. A sample of stannous chloride which is not completely soluble

in water probably contains the *basic chloride.* When a little hydrochloric acid is added to the mixture the basic salt dissolves and a clear solution is obtained :

$$Sn(OH)Cl + HCl = SnCl_2 + H_2O.$$

When stannous chloride or its aqueous solution is exposed to the air, oxidation takes place with the formation of *stannic chloride,* especially in the presence of hydrochloric acid :

$$2\ SnCl_2 + 4\ HCl + O_2 = 2\ SnCl_4 + 2\ H_2O.$$

Thus the chief impurities of stannous chloride are stannous oxychloride and stannic chloride.

Qualitative Examination.—The qualitative analysis of stannous chloride is carried out in the same way as in the analysis of stannic chloride.

Insoluble Matter.—Any insoluble residue obtained on dissolving the sample in water is filtered off, dried and weighed. Determination of the *tin* and *chlorine* contents of the insoluble residue is made by the methods already described.

Determination of Tin.—The determination of the divalent tin present in stannous chloride may be carried out directly by titration with iodine or indirectly by titration with potassium permanganate or titanous chloride in the presence of ferric salts.

(1) *Iodine Titration.*—About 0·25 grm. of the sample (or its equivalent in the form of an aqueous solution) is dissolved in water acidified with hydrochloric acid. 50 c.c. of a 10 per cent. solution of potassium sodium tartrate (Rochelle salt) and 50 c.c. of a 10 per cent. solution of sodium hydrogen carbonate are added. The mixture is then titrated with a decinormal solution of iodine (1 c.c. $N/10$ iodine $\equiv$ 0·00594 grm. Sn) using a starch solution as indicator and titrating until a permanent blue coloration is produced.

(2) *Titration with Potassium Permanganate.*—0·5 grm. of the sample is dissolved in water acidified with hydrochloric acid. A small excess of ferric chloride solution is then added to oxidise the stannous chloride. The resulting ferrous chloride is then determined by titration with a decinormal solution of potassium permanganate. 1 c.c. $N/10$ $KMnO_4 \equiv$ 0·00594 grm. Sn.

Determination of Stannic Chloride in Stannous Chloride.—Commercial stannous chloride may contain stannic chloride, the amount of which can be determined in the manner described under the analysis of stannic chloride after oxidation of the tin present in the stannous condition by means of potassium chlorate or nitrate. By subtracting the tin present in the *stannous condition* from the *total tin* so found, the percentage of tin present in the form of the *stannic salt* is given.

Determination of Chlorine.—The determination of the *total chlorine* present is performed on the solution of the sample after oxidation and precipitation of the tin in the same way as for the determination of the chlorine in samples of stannic chloride. The chlorine so found is apportioned between the stannous and stannic tin and any excess expressed in terms of free *hydrochloric acid.* If the chlorine present is less than that corresponding to the tin content of the sample, determination of the other acids present should be made.

Antimony.

Antimony Potassium Tartrate, $(KSbO\,.\,C_4H_4O_6)_2\,.\,H_2O$, is obtained by mixing antimony trioxide with an aqueous solution of potassium hydrogen tartrate, filtering and crystallising the solution. It is a colourless crystalline substance, soluble in 17 parts of water and almost insoluble in 90 per cent.

alcohol. It should be free from *potassium hydrogen tartrate*, the presence of which is indicated if the sample effervesces when treated with sodium bicarbonate. Ammonium salts, copper, iron, chlorides and sulphates should be absent. The percentage of *antimony* is 36·17. This may be determined by titration with decinormal iodine solution. If 0·5 grm. of the substance is dissolved in 25 c.c. of water together with 5 grms. of potassium hydrogen tartrate and 1·5 grms. of sodium bicarbonate, from 29·8 to 30·2 c.c. of decinormal iodine solution should be required. The titration is carried out in the presence of starch, the end-point being the production of blue iodide of starch. The addition of potassium hydrogen tartrate is to prevent any separation of antimonious acid during the titration. The reaction is represented by the equation

$$KSbO \,.\, C_4H_4O_6+6NaHCO_3+I_2=Na_3SbO_4+2NaI+KNaC_4H_4O_6+3H_2O+6CO_2.$$

Hence 1 c.c. $N/10$ iodine solution $\equiv$ 0·0166 grm. of potassium antimony tartrate or 0·006 grm. of antimony.

Titanium.

Titanium forms two classes of salts, viz. *titanous* and *titanic salts*, corresponding to titanous oxide, Ti_2O_3, and titanium dioxide, TiO_2. The titanous salts are very powerful reducing agents and are used as stripping agents and in the volumetric determination of dyestuffs. The principal compounds are *titanous chloride*, $TiCl_3$, and *titanous sulphate*, $Ti_2(SO_4)_3$. Owing to the readiness with which they are oxidised they are sold only in solutions which must be preserved carefully from contact with air. Both form dark purplish-coloured solutions which contain also *free acid*. *Titanium potassium oxalate* is used in tanning as a mordant and for fixing tannic acid.

Qualitative Reactions.—When titanous salts are treated with an alkali, such as ammonia, a black precipitate of titanous hydroxide, $Ti_2(OH)_6$, is formed which, on exposure to the air, gradually becomes white, hydrogen being evolved simultaneously; the white precipitate consists of *titanic hydroxide* or titanic acid, $Ti(OH)_4$:

$$Ti_2(OH)_6 + 2\,H_2O = 2\,Ti(OH)_4 + H_2.$$

If tannic acid be added to a solution of a titanous salt, an orange-coloured precipitate of *titanium tannate* is produced. The most delicate test, however, is the formation of a deep yellow colour with *hydrogen peroxide*; this test may be used also for the detection of hydrogen peroxide. Chromic, vanadic and molybdic acids give a similar reaction, hence their absence must be ensured before making the test. Small quantities of iron do not affect the reaction, but if iron is present in large amounts the natural colour of the solution masks the yellow tint. If the iron is precipitated with phosphoric acid no trouble is experienced. The solution to be tested should contain at least 5 per cent. of sulphuric acid. The reaction is extremely delicate, detecting as little as 0·00005 grm. of TiO_2 in 50 c.c.

The action of titanous salts with *copper sulphate* is delicate and characteristic, the reduction taking place in two stages. First, cuprous sulphate is formed, and then metallic copper, in accordance with the equation

$$CuSO_4 + Ti_2(SO_4)_3 = Cu + 2\,Ti(SO_4)_2.$$

Determination of Titanium.—In the absence of aluminium or other metals of the same group, titanium may be determined gravimetrically by boiling the solution with a slight excess of ammonia until the titanous oxide first precipitated

is converted into *titanic acid*, $Ti(OH)_4$. This is filtered off, washed, ignited to TiO_2, and weighed. ($TiO_2 \times 0{\cdot}599 = Ti$).

Acetic acid containing ammonium acetate may be substituted for ammonia and has the advantage that small quantities of aluminium are held in solution.

Titanous salts may be determined *volumetrically* by means of a standard solution of *ferric alum*, potassium sulphocyanide being used as indicator. The solution is acidified with hydrochloric acid, an excess of potassium sulphocyanide solution added and the iron solution run in from a burette until a red colour due to ferric sulphocyanide is produced. *Titanic salts* can be titrated in a similar manner after reduction. Each 47·9 parts of titanium as titanous salt reduce 56 parts of iron. Small quantities of titanium may be estimated *colorimetrically* by means of hydrogen peroxide. A standard solution of titanous sulphate is required; Treadwell (*Analytical Chemistry*, Vol. II, p. 101) prepares this in the following manner: Potassium titanic fluoride is purified by recrystallisation and ignited gently. A quantity corresponding to 0·2 grm. of TiO_2 (0·600 grm.) is weighed out and treated in a platinum crucible several times with a little water and concentrated sulphuric acid, the excess acid being driven off by gentle ignition. The residue is dissolved in a little concentrated sulphuric acid and the liquid diluted to 100 c.c. with 5 per cent. sulphuric acid (1 c.c. $\equiv$ 0·002 grm. TiO_2). The solution to be tested is placed in a Nessler cylinder, acidified with sulphuric acid, a little 10-volume hydrogen peroxide added and the solution made up to a definite volume. The colour is matched in the usual way by trial experiments with the standard titanium solution. Hydrofluoric acid must not be present, and hydrogen peroxide made by treating barium peroxide with hydrofluosilicic acid must not be used; that obtained by dissolving pure sodium peroxide in dilute sulphuric acid is suitable.

CHAPTER XVII.

NITRO-COMPOUNDS, AMINES AND PHENOLS.

Nitro-compounds.

NITRO-COMPOUNDS are as a rule insoluble in water, but dissolve in ether, and are in some cases volatile in steam. All nitro-compounds give an intense blue colour when treated with a solution of diphenylamine in sulphuric acid. When reduced with tin and hydrochloric acid, the hydrochloride of the corresponding amine is obtained. The percentage of *nitrogen* may be determined by the modified Kjeldahl method described in Chapter V.

The Determination of Nitro-compounds.—Two methods are available for the quantitative analysis of nitro-compounds, viz. titration with titanous chloride or with potassium bromate.

Titanous Chloride Method.—This method was described by Knecht and Hibbert (*New Methods of Volumetric Analysis*) and depends upon the fact that nitro-compounds are reduced quantitatively to *amines* by titanous chloride or sulphate under suitable conditions. The preparation of titanous chloride solution and the method of titration have been described in Chapter IV. A weighed quantity of the compound is dissolved in water or acid, or, when insoluble, it may be sulphonated first by treatment with concentrated sulphuric acid. Some nitro-compounds, such as nitrobenzene, are not sulphonated readily, and these may be dissolved in alcohol. The solution of the nitro-compound is added to a known excess of standard titanous chloride solution acidified with hydrochloric acid and carbon dioxide passed into the titration flask. The mixture is boiled to complete the reduction, then cooled, and the unused titanous chloride determined by titration with standard iron alum solution, as described in Chapter IV.

Callan and Henderson (*J.S.C.I.*, 1922, 156 T) found that there were two sources of error to be considered. Firstly, many nitro-compounds are volatile in steam. When this is the case, reduction should be carried out in a flask fitted with a short ground-in water condenser about 9 inches long, a stream of carbon dioxide being supplied by a narrow glass tube passing through the condenser to within a few inches of the surface of the liquid. The second source of error is chlorination of the nitro-compound, but this does not occur when titanous sulphate is used. When precautions are taken to avoid these sources of error, nitro-compounds are reduced quantitatively by titanous salts. The use of recrystallised *para*nitroaniline is recommended for the standardisation of the titanous sulphate solution. The substance is crystallised first from alcohol and then from water, and the final crystals should melt at 149°–149·5° C.

Potassium Bromate Method.—Callan and Henderson (*loc. cit.*) found that nitro-compounds which contain either amino- or hydroxyl-groups can in most cases be determined accurately by titration with standard potassium bromate solution (*vide* Amines). A weighed quantity of the substance is dissolved and the solution diluted to about 250 c.c. in a stoppered bottle, after which 10 c.c.

of 20 per cent. potassium bromide solution and 10 c.c. of pure hydrochloric acid are added. The potassium bromate solution is then run in slowly until a drop of the liquid gives a reaction with starch-iodide paper which persists for 2 to 4 minutes after the last addition of the bromate. The last test with the starch-iodide should not be made immediately after the addition of the bromate, although in the earlier stages this is immaterial. The following are examples of this method :—

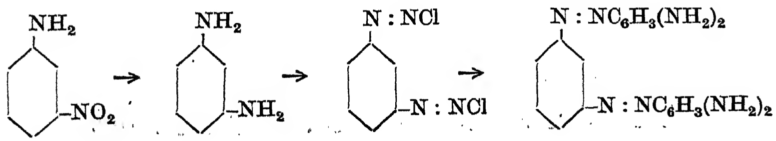
Paranitroaniline.—From 3 to 4 grms. are dissolved in 30 c.c. of concentrated hydrochloric acid and 50 c.c. of water. The solution is made up to 500 c.c. and 50 c.c. titrated. At 60°–70° C. the titration is quantitative and the end-point sharp, provided that no considerable excess of hydrochloric acid is used. Each molecule of *para*nitroaniline takes up 2 atoms of bromine.

Picric Acid does not absorb any bromine even at 60°–70° C., but 1 : 2 : 4-*dinitrophenol* takes up one atom per molecule, thus affording a method of determining dinitrophenol in the presence of picric acid.

Paranitroaniline, $C_6H_4<^{NH_2}_{NO_2}$. The nitroanilines are yellow crystalline substances which are only slightly soluble in water. They dissolve in boiling hydrochloric acid with the formation of the hydrochloride, $C_6H_4NO_2NH_2.HCl$, which crystallises out when the solution is cooled. The differences between the three isomeric forms are shown in the following table given by Allen (*Commercial Organic Analysis*, Vol. V, p. 545) :

	Ortho.	*Meta.*	*Para.*
Appearance and crystalline form, .	Orange-yellow needles.	Long yellow needles.	Long yellow needles.
Taste, . . .	—	Sweet, burning.	Nearly tasteless.
Melting-point, . .	71·5° C.	110° C.	147° C.
Volatility, . .	Distils with steam.	Distils with steam. Sublimes at 100° C.	Not volatile with steam.
Salts, . . .	Very unstable.	Fairly stable.	Unstable.
Behaviour when boiled with strong sodium hydroxide solution, . .	—	—	Forms *p*-nitrophenol.

The purity of a sample of *para*nitroaniline may be ascertained by taking the melting-point, and proving the absence of the *meta*-compound by the following test (Allen, *loc. cit.*) : 0·25 grm. of the sample is heated with zinc and hydrochloric acid until decolorised, the solution then filtered, diluted to 50 c.c., and 2 or 3 drops of a dilute solution of sodium nitrite added. If the *meta*-compound is absent a yellow colour is produced, but in its presence a brown colour due to Bismarck Brown is formed, thus :



The percentage of the nitro-compound present may be determined by the bromate method already described or by titration with standard sodium nitrite solution (*vide* Amines), potassium iodide-starch paper being used as indicator.

Amines.

Amines are usually insoluble in water, but form soluble salts when treated with acids. They give also crystalline double chlorides with platinum chloride. In the case of aromatic amines the percentage of *nitrogen* may be determined by the Kjeldahl method.

Primary Amines are distinguished from secondary and tertiary amines by the following reactions :

(1) When mixed with chloroform and alcoholic potassium hydroxide and warmed, they give *carbylamines*, which can be recognised by their characteristic smell :

$$C_2H_5NH_2 + CHCl_3 + 3\ KOH = C_2H_5NC + 3\ KCl + 3\ H_2O.$$

(2) When an *aliphatic* primary amine is treated with nitrous acid, *nitrogen* gas is evolved and the corresponding alcohol formed :

$$C_2H_5NH_2 + HO\ .\ NO = C_2H_5OH + N_2 + H_2O.$$

Aromatic primary amines, when treated with nitrous acid and hydrochloric acid, give *azo-compounds* :

$$C_6H_5NH_2 + HO\ .\ NO + HCl = C_6H_5N : NCl + 2\ H_2O.$$

These azo-compounds can be coupled with β-naphthol to give a dyestuff, and when they are boiled with water they are decomposed with the formation of a phenol and nitrogen :

$$\begin{aligned} C_6H_5N : NCl + C_{10}H_7OH &= C_6H_5N : NC_{10}H_6OH + HCl\ ; \\ C_6H_5N : NCl + H_2O &= C_6H_5OH + N_2 + HCl. \end{aligned}$$

(3) Primary amines react with *acid chlorides*. In the case of aromatic amines the products are solid crystalline compounds, purified easily by recrystallisation and having definite melting-points. Acetanilide is an example :

$$C_6H_5NH_2 + CH_3COCl = C_6H_5NH.OCCH_3 + HCl.$$

Secondary Amines give *nitrosamines* when treated with nitrous acid :

$$C_6H_5NHC_6H_5 + HO\ .\ NO = C_6H_5N(NO)C_6H_5 + H_2O.$$

Nitrosamines can be recognised by Liebermann's reaction. A little of the substance is mixed with phenol and a drop or two of concentrated sulphuric acid added. A deep green colour is produced, which becomes red on dilution with water and blue on neutralising with sodium hydroxide. Secondary amines react with *acid chlorides*, thus :

$$C_6H_5NHC_6H_5 + CH_3COCl = C_6H_5N(OCCH_3)C_6H_5 + HCl.$$

Tertiary Amines do not react with either nitrous acid or acid chlorides.

The Determination of Amines.—The only general methods applicable to the determination of amines are titration by means of potassium bromate solution or with a standard solution of sodium nitrite.

Titration with Standard Potassium Bromate.—This method was used in the case of aniline by Reinhard in 1893 and was modified by Dobriner and Schranz (*Zeit. Anal. Chem.*, 1895, **34**, 734-740). It is applicable to both aliphatic and aromatic compounds, and depends on the fact that whilst the direct action of bromine is slow and often incomplete, when bromination is brought about by means of nascent bromine, liberated by the interaction of potassium bromate and potassium bromide in the presence of hydrochloric acid, in many cases a rapid and quantitative reaction takes place. In practice, the potassium bromide and hydrochloric acid are added in excess to the solution of the substance to be titrated, and the potassium bromate solution is run in from a burette, the end-point being the presence of free bromine, found by spotting on to starch-iodide paper. Alternatively, an excess of potassium bromate solution may be added and then potassium iodide, the liberated iodine being determined by titration with sodium thiosulphate solution.

According to Callan and Henderson (*J.S.C.I.*, 1922, T 161) the bromination of aromatic compounds is governed chiefly by (*a*) the orientation of the substituent groups, (*b*) the nature of these groups, (*c*) the temperature of the reaction. Vaubel showed that in the case of amines and phenols the bromine enters the ring in the *ortho* or *para* position, but never in the *meta* position. If there is no unoccupied *ortho* or *para* position bromination does not take place, unless these positions are occupied by carboxyl or sulphonic acid groups, in which case the group is split off and replaced by a bromine atom. Thus *ortho*- and *para*-cresols both take up two atoms of bromine, whilst *meta*-cresol is able to take up three atoms. Aniline and sulphanilic acid combine with three atoms of bromine, forming the same compound, tribromoaniline. In the case of sulphanilic acid the reaction is dependent on the temperature and it is possible to determine exactly the intermediate stage at which dibromosulphanilic acid is the only product. *Meta*-diamines, *meta*-dihydroxy-compounds and *meta*-aminophenols take up bromine quantitatively, whilst with *para*-diamines and *para*-dihydroxy-compounds oxidation occurs.

In the naphthalene series 2-naphthol-3 : 6-disulphonic acid ("R"-salt) absorbs bromine quantitatively at room temperatures, whilst the isomeric "G"-salt, 2-naphthol-6 : 8-disulphonic acid does not take up bromine at all at this temperature.

The temperature of titration has a considerable effect in determining the speed of bromination and also, as in the case of anthranilic acid, the extent of bromination. The optimum temperature should be determined for each substance, but in practically all cases in which the method is suitable, room temperature will be found convenient.

Callan and Henderson recommend the following method of determination: 0·2–0·5 grm. of the amino-compound is dissolved in 200–250 c.c. of water with a slight excess of hydrochloric acid. In the case of phenols, sodium hydroxide is used, whilst acids may be dissolved in water, adding a little sodium hydroxide if necessary. To the solution are added 10 c.c. of 20 per cent. potassium bromide solution and 10 c.c. of concentrated hydrochloric acid. When the substance is insoluble in water, dilute acid and dilute alkali, glacial acetic acid may be used, diluting with water towards the end of the titration. The potassium bromate solution ($N/5$) is then run in until a drop of the liquid gives a reaction with starch-iodide paper which persists for 2 to 4 minutes. The final test with the

starch-iodide should *not* be made immediately after the addition of the bromate solution.

The following table gives the conditions of titration for some common amines :

Amine.	Temperature of Titration.	Atoms of Bromine Absorbed per Molecule.
Aniline,	Room temperature.	3
o- and *p*-Toluidines,	do.	2
m-Toluidine,	do.	3
Dimethylaniline,	40–50° C.	2
do.,	60–70° C.	3
Sulphanilic acid,	15° C.	2
do.,	60–70° C.	3
p-Nitroaniline,	60–70° C.	2
Diphenylamine,	60–70° C.	4

The titration of aniline with potassium bromate is preferable to determination by means of standard sodium nitrite solution. In the case of the toluidines the method can be applied to mixtures of the *ortho*- and *para*-compounds with aniline. Diphenylamine is dissolved in glacial acetic acid and diluted with water towards the end of the titration.

With sulphanilic acid two atoms of bromine are taken up at low temperatures, but at 60–70° C. three are absorbed, with the elimination of the sulphonic acid group and precipitation of tribromoaniline. Callan and Henderson state that it is possible to isolate readily the stages at which two and three atoms are absorbed, the precipitation of tribromoaniline acting as an indicator and showing the commencement of the second stage. At 30°–40° C. a distinct reaction with starch-iodide paper, persisting for 30 seconds after the last addition of the bromate, marks the end of the first part of the reaction, after which the formation of tribromoaniline is immediately evident. The titration may be made then either at 30–40° C. or at 60–70° C.

Titration with Standard Sodium Nitrite.—This method depends upon the reaction

$$C_6H_5NH_2 + HO.NO + HCl = C_6H_5N : NCl + 2\,H_2O.$$

A weighed quantity of the amine is dissolved in an excess of hydrochloric acid, the solution diluted with water and some ice added. A standardised solution of sodium nitrite is then run in slowly from a burette until a drop of the liquid gives a blue colour with starch-iodide paper. The titration must be carried out slowly, time being allowed after each addition of nitrite solution for the formation of the azo-compound. The instability of nitrous acid even at 0° C. is considerable; Jones and Lee (*Ind. Eng. Chem.*, 1924, **16**, 948) state that by adding nitric acid this decomposition is inhibited. They recommend also the addition of an excess of the sodium nitrite solution and back-titration by means of a standard solution of *p*-nitroaniline, which reacts according to

$$C_6H_5N : NCl + C_6H_4{<}^{NO_2}_{NH_2} = HCl + C_6H_5N : NC_6H_3{<}^{NO_2}_{NH_2}.$$

A decinormal sodium nitrite solution is made by dissolving **6·9 grms.** of the salt in one litre of water and titrating against decinormal potassium permanganate.

Aniline, $C_6H_5NH_2$.—Pure aniline is a colourless liquid, with a characteristic smell. Its boiling-point is 183·7° C. and its specific gravity 1·0265 to 1·0267 at 15° C. It is slightly soluble in water (3 parts per 100), but dissolves readily in alcohol, ether and chloroform. It unites directly with acids, forming soluble and crystalline salts. It may be identified by the following tests:

(1) When it is boiled in a test-tube and a glass rod moistened with hydrochloric acid is held in the vapour, dense white fumes of *aniline hydrochloride* are produced.

(2) When treated with *bleaching powder* solution a violet colour is formed.

(3) One drop of the liquid is placed on a porcelain slab and about six drops of concentrated sulphuric acid are added and the liquids well mixed with a glass rod. A very small quantity of finely powdered *potassium bichromate* is then sprinkled over the surface of the mixed liquids, when a beautiful blue coloration will be produced in the presence of aniline.

(4) A few drops of the liquid are dissolved in a small quantity of dilute hydrochloric acid and a little of a solution of sodium nitrite added. The mixture is allowed to stand in the cold for 15–30 minutes and then gently heated. If aniline is present a brisk evolution of *nitrogen* will take place, accompanied by the characteristic odour of phenol:

$$R.NH_2 + NaNO_2 + 2\,HCl = 2\,H_2O + NaCl + RN : NCl,$$
$$RN : NCl + H_2O = R.OH + N_2 + HCl.$$

The reaction is common to other aromatic amines, and the resulting mixture should be examined for *phenol* (*q.v.*).

Commercial aniline may contain *toluidine.* This may be detected by the fact that it yields Magenta when oxidised, whereas pure aniline does not. The following test (Allen, *Commercial Organic Analysis*, Vol. V, p. 564) may be employed: 5 c.c. of the sample are mixed with an equal volume of a concentrated solution of arsenic acid containing about 75 per cent. of As_2O_5 and having a density of 2·04. The mixture, contained in a small flask or long test-tube, is immersed in a paraffin bath heated to 180° C. When the action is complete the contents of the tube acquire a bronze appearance and no longer intumesce. The product is treated with boiling water. If the sample contained toluidine, arsenate of rosaniline dissolves and the liquid will have an intense crimson colour. Neither pure aniline nor pure toluidine gives this reaction. If commercial aniline be mixed with a little solid Magenta, a few drops of glacial acetic acid added and the whole heated to 180° C., ammonia is given off and blue triphenylrosaniline is formed; toluidine treated in the same way gives a purple dyestuff, whilst a mixture of the two gives intermediate colours.

Analysis.—The specific gravity of commercial samples at 15° C. should be between 1·0260 and 1·0267. When distilled, 95 per cent. should come over between 180° C. and 185° C. Water should be absent, and 10 c.c. of the oil should give a clear solution when mixed with 50 c.c. of water and 40 c.c. of hydrochloric acid.

Distillation Range and Moisture Content.—The determinations of the moisture content and distillation range of the sample are carried out by the method of Liebmann and Studer (*J.S.C.I.*, 1899, **18,** 110), in which they are performed in one operation. 100 c.c. of the oil are distilled from an ordinary distilling flask with side tube and the first 10 c.c. of distillate collected separately in a narrow stoppered graduated 15 c.c. cylinder. A few pieces of platinum wire should be introduced into the flask to promote regular ebullition, and the neck of the flask should be closed by a cork carrying a thermometer reading to 0·1–0·2° C. and passing down the neck of the flask to a depth such that the top of the bulb

is level with the side tube of the flask. The flask and contents should be heated by means of a small direct flame, such as that obtained from a microburner. 1 c.c. of a saturated brine solution is added to the 10 c.c. of distillate collected in the foregoing manner, the mixture well shaken, and then allowed to stand until separation into two layers is complete. The volume of the aqueous brine layer is then read and the increase in volume over that of the brine added is noted. This increase in volume, plus a correction equivalent to 0·3 per cent. of the volume increase (arising from the moisture content of aniline oil in equilibrium with a saturated brine solution), gives the percentage of *water* by volume present in the original sample.

In determining the distillation range the temperature at which distillation commences is regarded as that at which the first drop of condensed vapour forms at, or drops from, the end of the bulb of the thermometer. The temperature recorded by the thermometer is carefully observed at intervals corresponding to the collection of each 10 c.c. of distillate, the rate of distillation being regulated to one drop per second. When the first 10 c.c. of distillate have been collected for the moisture determination, the receiver employed should be replaced by a 100 c.c. measuring cylinder. The distillation should be continued to dryness and the final temperature of the vapours noted. If any sudden increase in temperature takes place during the distillation, the volume of distillate collected up to that point should be noted and recorded.

Solubility in Hydrochloric Acid.—The examination of the solubility of samples of aniline oils in hydrochloric acid for the detection of insoluble oils is of the highest importance and must never be neglected. In carrying out this test it is essential to use a dilute solution, since concentrated solutions of aniline hydrochloride act as a solvent for many of the impurities associated with aniline oils. According to Knecht, Rawson and Loewenthal (*Manual of Dyeing*, 1920, Vol. II, p. 808), 10 c.c. of the sample should be dissolved in an equal volume of hydrochloric acid and the solution then diluted to 100 c.c. An oily or solid precipitate, or even a cloudiness, denotes the presence of non-basic bodies, such as nitrobenzene, naphthalene, etc. (these substances being recognisable by their odour). The presence of nitrobenzene may be confirmed or detected by violently shaking the sample of the oil; if nitrobenzene is present the foam produced by the agitation will have a distinctly yellow colour. Since nitrobenzene boils at 209° C. it will be found in the last fractions obtained in the distillation test or remain in the flask. If these last fractions are dissolved in hydrochloric acid and distilled with steam the nitrobenzene can be separated.

Determination of Sulphur.—The detection of sulphur compounds, which are usually present in technical aniline oils, is a simple operation based upon the fact that the sulphur compounds present are decomposed on boiling with production of hydrogen sulphide. The distillation of the sample for the determination of the moisture content and distillation range affords an opportunity to determine whether the quantity of sulphur present may be neglected or should be tested by fixing a piece of lead acetate paper at the end of the condenser in such a manner that it is exposed to any vapour issuing from the condenser but does not come into contact with the distillate. If the lead acetate paper is only coloured a light brown, only traces of sulphur are present, but if the coloration becomes deep black the sulphur present should be determined by the method of Liebmann and Studer (*ibid.*): A weighed quantity of the sample is boiled under a reflux condenser for several hours, during which time a stream of carbon dioxide is bubbled through the liquid and subsequently washed with an accurately-measured volume of a decinormal solution of silver nitrate contained in an absorption bulb or Dreschler cylinder.

On completion of the operation the contents of the absorption apparatus are filtered through a Gooch crucible and the apparatus thoroughly rinsed, the rinsings also being passed through the Gooch crucible. The residue of silver sulphide remaining in the Gooch crucible is then washed and the washings added to the filtrate. The silver remaining in the collected filtrate and washings is determined by titration with potassium sulphocyanide.

Phenols.

Phenol (*Carbolic Acid*), C_6H_5OH, is a coal tar product found in the fraction distilling between 170° and 230° C., and is recovered therefrom by treatment of the distillate with caustic soda solution; the undissolved oils are separated and the remaining aqueous alkaline liquid acidified with sulphuric acid, when the phenol is precipitated and rises to the surface, forming an oily layer. Phenol is a colourless solid and crystallises in needle-shaped crystals melting at 41° C. to a colourless liquid of boiling-point 182° C. When exposed to the air it absorbs moisture, forming a hydrate of the composition $(C_6H_5OH)_2.H_2O$, melting at 17·2° C.

Carbolic acid dissolves in water to the extent of 1 in 11 at 15° C. but other phenols are, as a rule, much less soluble or insoluble. They are all dissolved, however, by a solution of sodium hydroxide, with the formation of the corresponding phenate, R.ONa. These phenates are not produced with sodium carbonate, being decomposed by carbonic acid in accordance with the equation

$$C_6H_5ONa + H_2CO_3 = C_6H_5OH + NaHCO_3.$$

The phenates are hydrolysed by water, a considerable excess of alkali being required to keep them in solution.

Many phenols can be volatilised with steam and may be separated from mixtures containing them by this means. Other volatile compounds should first be removed by distillation in the presence of excess of sodium hydroxide. The phenols are soluble as a rule in organic solvents. All give characteristic precipitates when treated with excess of bromine water, consisting of substitution products. Similar bodies are formed also with iodine.

Qualitative Reactions.—(1) When a little dilute *ferric chloride* solution (10 per cent.) is added to a solution of phenol, a violet colour is produced. In the presence of from 2·5 to 2·7 per cent. of alcohol this colour is not obtained.

(2) If an excess of *bromine water* be added to a solution containing phenol, a yellow crystalline precipitate of tribromophenol, $C_6H_2Br_3OH$ is formed.

(3) When a solution of phenol is mixed with about one per cent. of nitric acid and the mixture poured on to the surface of concentrated sulphuric acid, a red colour is produced at the junction of the two liquids.

(4) *Liebermann's nitroso-reaction* may be employed for the detection of phenol. The latter is mixed with concentrated sulphuric acid and a little sodium nitrite solution is added. An intense green colour is produced, which becomes red on dilution with water, and blue when neutralised with sodium hydroxide.

(5) When an aqueous solution of phenol is treated with a little ammonia solution and some clear *bleaching powder* solution is added and the mixture warmed, a blue colour is produced.

In order to distinguish between phenol and cresols, Arnold and Werner (*Apoth. Zeit.*, 1905, **20,** 925) employed the following tests:

(*a*) To 10 c.c. of the test solution are added 10 c.c. of potassium hydroxide

solution, 10 c.c. of alcohol and 1 drop of aniline. The mixture is shaken and 5 drops of hydrogen peroxide and 10 drops of sodium hypochlorite are added and the whole again shaken. Phenol gives a dirty red transient colour, changing to yellow, *o*- and *m*-cresols and tricresol a violet colour changing at once to green, and *p*-cresol a violet colour which disappears at once.

(*b*) With ferric chloride *o*-cresol gives a blue colour, changing rapidly to green; phenol, *m*-cresol and tricresol give a violet colour, and *p*-cresol a blue colour.

(*c*) On warming with a little phthalic acid and 5 drops of sulphuric acid, *m*-cresol gives a cherry-red colour, phenol and tricresol give a dark red colour, *o*-cresol a cherry-red colour, and *p*-cresol an orange colour. On diluting with water and making alkaline with sodium hydroxide, the phenol gives a magenta colour, the *o*-cresol and tricresol a violet-red colour, the *m*-cresol a bluish-violet colour, and the *p*-cresol a yellowish colour.

(*d*) A dilute ammoniacal solution of *p*-cresol, when boiled and treated with bromine water, gives no coloration; phenol and *o*-cresol give a blue colour, and tricresol a bluish-green colour.

(*e*) If a trace of potassium nitrate be added to a solution of a little of the substance in sulphuric acid, a dark-red colour is produced in the case of *p*-cresol, the other phenols giving an emerald-green colour.

(*f*) When diluted with water and treated with excess of ammonia, *p*-cresol gives a yellow colour and the other phenols a green colour.

The *p-nitrobenzyl ethers* of phenols crystallise readily and have definite melting-points. They are obtained by the action of *p*-nitrobenzyl bromide upon the sodium or potassium phenolates:

$$C_6H_4(NO_2)CH_2Br + NaOC_6H_5 = C_6H_4(NO_2)CH_2OC_6H_5 + NaBr.$$

Reid (*J. Amer. Chem. Soc.*, 1917, **39,** 304) utilises this reaction in the following manner: 25 c.c. of a solution of 0·2 *N* sodium hydroxide in 95 per cent. alcohol are introduced into a 100 c.c. flask and a moderate excess of the phenol added (this will generally be about 1 grm. for phenols of molecular weight less than 200). 1 grm. of *p*-nitrobenzyl bromide is then added to the solution and the mixture refluxed for 60 mins., the progress of the reaction being indicated by the precipitation of the sodium bromide. 5–10 c.c. of water are then added to dissolve the bromide and the solution rapidly cooled whilst vigorously shaken to cause the formation of small crystals. During the separation of the crystals the mixture should be kept just alkaline to prevent the separation of unchanged phenol, which might contaminate the *p*-nitrobenzyl ether. The ether is filtered off, dissolved in boiling 95 per cent. alcohol, and again thrown out by the cautious addition of water. The following preparations have been made by Reid (*loc. cit.*):

Ether.	Melting-point.
Phenyl-*p*-nitrobenzyl ether, . .	91° C.
o-Cresyl-*p*- ,, . .	89·7° C.
m-Cresyl-*p*- ,, . .	51·0° C.
p-Cresyl-*p*- ,, . .	88·0° C.
Vanillyl-*p*- ,, . .	124·5° C.

Determination of Phenol.—The determination of phenol is complicated by the fact that all phenolic compounds have similar properties. Whilst the

identification or determination of a single phenol is comparatively simple, the analysis of a mixture is very difficult.

Many methods have been proposed for the determination of phenol, the most convenient being based upon the formation of bromine compounds. The standard *bromide-bromate solution* may be used: A weighed quantity of the phenol is dissolved in sodium hydroxide solution in a stoppered bottle of about 250 c.c. capacity. A measured volume of the bromide-bromate solution is then run in, followed by sufficient hydrochloric acid to liberate the bromine, which must be present in considerable excess. The bottle is then placed in a dark cupboard for half an hour. Potassium iodide is then added and the liberated iodine titrated with decinormal sodium thiosulphate solution, each cubic centimetre of which corresponds to 0·00157 grm. of phenol.

Messinger and Vortmann recommended the direct use of *iodine solution*: About 3 grms. of the sample are dissolved in sodium carbonate solution and the solution diluted to 500 c.c. A portion (10 c.c.) of this solution is heated to 60° C. and an excess of decinormal iodine solution added. The mixture is cooled, acidified with sulphuric acid and made up to 500 c.c. The excess of iodine is then determined by titration with decinormal sodium thiosulphate solution. The iodine absorbed, multiplied by 0·1235, gives the phenol present.

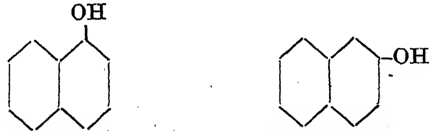
Phenols may be determined also by means of a solution of *diazotised para-nitroaniline* (Riegler, *Ann. Chim. Appl.*, 1901, **6**, 231). When phenol is treated with this solution in the presence of sodium hydroxide the following reaction takes place:

$$C_6H_4<^{N:NCl}_{NO_2} + C_6H_5ONa + NaOH = C_6H_4<^{N:N.C_6H_4.ONa}_{NO_2} + NaCl + H_2O.$$

On adding sulphuric acid drop by drop, an insoluble colouring matter, $C_6H_4<^{N:N.C_6H_4.OH}_{NO_2}$, separates, which is filtered off, dried and weighed. The weight of the precipitate multiplied by 0·3868 gives the phenol present, but a correction of 0·002 grm. per 100 c.c. of liquid used is made for the slight solubility of the compound.

The Determination of Phenol in Soap.—The determination of phenol in soap may be carried out by the following method: A weighed quantity of the soap is dissolved in water and a little sodium hydroxide solution added. Salt is then introduced until the soap is precipitated. The liquid is then made up to a definite volume with brine and filtered. The phenol is determined in a portion of the filtrate by the bromide-bromate method.

***α*- and *β*-Naphthols.**—Naphthols are monohydroxy-derivatives of naphthalene and belong to the phenol class of hydroxy-compounds. The two isomeric naphthols are obtained when the corresponding naphthalene sulphonic acids are fused with sodium or potassium hydroxide; they are represented by the formulæ



α-Naphthol. *β*-Naphthol.

It is necessary for many purposes that naphthols should be free from impurities

and not contaminated with one another. The general characteristics of α-naphthol and β-naphthol are given in the following table :

	α-Naphthol.	β-Naphthol.
Crystalline form,	Monoclinic needles.	Monoclinic plates.
Solubility in cold water,	Slightly soluble.	Slightly soluble.
,, ,, hot water,	Slightly soluble.	Soluble.
,, ,, alcohol,	Soluble.	Soluble.
,, ,, ether,	Soluble.	Soluble.
Melting-point,	95° C.	122° C.
Boiling-point,	278–280° C.	286° C.
Melting-point of acetate,	46° C.	61° C.

Qualitative Tests.—A great many reactions have been proposed for the detection of and distinction between α-naphthol and β-naphthol. The following are the most important :

Hypobromite Test.—Saturated solutions of naphthols give characteristic colour reactions with a solution of sodium hypobromite. Callan (*J.S.C.I.*, 1925, 125 T) recommends the following procedure : 0·5 grm. of the naphthol is ground in a glass mortar with 10 c.c. of distilled water and the mixture allowed to stand for 15 minutes with occasional stirring. The mixture is then filtered and to the filtrate is added, drop by drop, 1 c.c. of a freshly prepared solution of sodium hypobromite, made by adding 5 c.c. of bromine to 130 c.c. of well-cooled 7 per cent. caustic soda solution. α-Naphthol gives a deep red-violet coloration or precipitate, whilst β-naphthol gives a yellowish solution.

Jorrisen's Test (*Ann. Chim. Appl.*, 1902, **7**, 217) : When 2 c.c. of potassium iodide-iodine solution, followed by excess of sodium hydroxide, are added to a solution of β-naphthol, a clear yellow solution is produced, but in the case of α-naphthol the mixture becomes turbid and violet. Arzberger (*Pharm. Post*, **35**, 753) gives the following modification of Jorrisen's test : 0·3 grm. of the sample is dissolved in 2 c.c. of alcohol, the solution diluted with 10 to 15 c.c. of water, allowed to stand for 15 minutes with frequent agitation, and filtered. From 10 to 12 drops of a 10 per cent. solution of potassium hydroxide are added to the filtrate, and then 1 to 4 drops of iodine-potassium iodide solution (prepared by dissolving 2 parts of potassium iodide and 1 part of iodine in 60 parts of water). Pure β-naphthol gives a yellow solution, α-naphthol a violet colour. The reaction may be made quantitative.

Denigès' Test (*Bull. Soc. Chim.*, 1916, **19**, 308).—Denigès employs the reactivity of tetravalent titanium with compounds containing a phenolic group as a means of distinguishing between α- and β-naphthols. A solution of titanic acid in sulphuric acid gives a bright green colour when mixed with a small quantity of α-naphthol and a blood red colour with β-naphthol. On dilution with acetic acid the green colour given by α-naphthol changes to reddish-violet, whilst the blood red colour of β-naphthol remains unchanged. The reaction may be applied as a ring test if the naphthol be dissolved in acetic acid and the titanic acid solution poured carefully down the side of the test-tube. Ethers of α- and β-naphthols give similar distinctive reactions with titanic acid.

The British Pharmacopoeia Test for β-naphthol is as follows : A hot saturated solution develops a blue fluorescence on the addition of one drop of ammonia. A cold saturated aqueous solution yields a white turbidity with chlorine water which, on addition of excess of ammonia, changes to a green or brown coloration. 0·1 grm. dissolved in 10 c.c. of boiling water gives, with ten drops of an aqueous

solution (1 in 30) of ferric chloride, a white precipitate, becoming brown, but not violet, the latter colour denoting the presence of α-naphthol.

Callan has increased the sensitiveness of the B.P. test in the following manner: 0·1 grm. of the sample is dissolved in 10 c.c. of boiling distilled water, the solution cooled and filtered. To the clear filtrate is added 0·5 c.c. of ferric chloride solution (1 in 30), drop by drop. After standing for about 15 minutes the colour of the precipitate is noted.

Chloral Hydrate Test.—This consists of mixing 0·1 grm. of the sample with 2·5 grms. of fused chloral hydrate and warming the mixture for 10 minutes. Another test is carried out with the addition of 5 drops of concentrated hydrochloric acid, and a third with the same amount of acid and a little zinc. The following colorations are obtained:

	α-Naphthol.	β-Naphthol.
Chloral hydrate, . . .	Intense ruby red; transparent, with fluorescence.	Pure blue; transparent, with no fluorescence.
,, and acid, .	Intense dark greenish-blue; not transparent.	Intense yellow; not transparent.
,, , acid and zinc,	Dark violet-blue; addition of water gives violet precipitate; alcohol solution reddish-violet with violet fluorescence.	Dark brown; addition of water precipitates a greasy body; alcohol solution yellow, with blue fluorescence.

In comparing the relative delicacy of the tests described it must be borne in mind that β-naphthol is less soluble in cold water than α-naphthol. Hence, where an aqueous extract is prepared, the sensitiveness of the test can be varied according to the relative amounts of water used in preparing the extract. In general the methods given will show positive results at concentrations of 0·1 per cent. of α-naphthol, or less, calculated on the percentage of β-naphthol.

The Determination of β-Naphthol.—β-Naphthol may be determined by titration with *iodine* and sodium thiosulphate in the following manner (Messinger and Vortmann, *Pharm. Jour. Trans.*, 1898, 91): 3 grms. of the sample are dissolved in a little water containing not less than 3·5 grms. of sodium hydroxide and the solution made up to 250 c.c. with water. A measured volume of this solution (10 c.c.) is placed in a small flask, heated to 55° C. and decinormal iodine solution added until the liquid shows a distinctly yellow colour, indicating the presence of excess of iodine. A dirty green precipitate may be produced when the mixture is shaken. The liquid is cooled, acidified with dilute sulphuric acid and diluted to 250 c.c. The excess of iodine is then determined by titrating a measured volume of this solution with decinormal sodium thiosulphate solution in the usual manner. Wilkie (*J.S.C.I.*, 1911, 403) showed that the reaction depends upon the excess of iodine present. Under the following conditions each molecule of naphthol absorbs two atoms of iodine: 2·44 grms. of naphthol are dissolved in 10 c.c. of $N/10$ sodium hydroxide, the solution diluted to 200 c.c., 10 c.c. of this solution diluted to 150 c.c. and 4 c.c. of $N/10$ sulphuric acid added followed by 20 c.c. of $N/10$ iodine solution. After heating for 15 minutes at 55° to 65° C., the mixture is acidified and the residual iodine determined by titration with thiosulphate.

The *bromide-bromate* method may be used also, each molecule of naphthol combining with two bromine atoms (1 c.c. $\frac{N}{10}$ bromine $\equiv$ 0·0072 grm. naphthol).

Determination of β-Naphthol in α-Naphthol.—Prochazka's method (*Analyst*, 1923, 568) may be used for this purpose: 0·36 grm. of the sample is dissolved in 40 c.c. of alcohol, cooled below 5° C. and titrated with a solution of *para*nitrodiazobenzene, 100 c.c. of which are equivalent to 1 grm. of sodium nitrite, until a red colour due to β-naphthol appears. The addition of the reagent must be made very slowly to allow time for coupling, the course of the reaction being followed by spotting the liquid on to filter paper moistened with dilute sodium hydroxide solution until a red colour due to *para*nitroaniline red appears. If unchanged α-naphthol be present, a blue line appears at the junction of the spots of titrated liquid and caustic soda, and the simultaneous coupling of α- and β-naphthols gives grey. A further quantity of the liquid is then added and the spotting test repeated, the process being continued until the red line due to *para*-nitroaniline red is produced. If the α-naphthol is pure, 17·25 c.c. of the diazo-solution would be required to convert it into the azo-compound.

Determination of α-Naphthol in the Presence of β-Naphthol.—The method of Prochazka (*J. Ind. Eng. Chem.*, 1923, **15**, 944) is generally used for this purpose: 1·44 grms. of the sample are dissolved in a mixture of 50 c.c. of alcohol, 3 c.c. of a solution of *para*nitrodiazobenzene and 0·03 grm. of sodium nitrite. The *para*nitrodiazobenzene solution contains the equivalent of 1 grm. of nitrite in 100 c.c.; it should contain only a very slight excess of nitrous acid and not a large excess of hydrochloric acid. If the amount of α-naphthol present is less than 0·5 per cent., the α-naphthol will be precipitated completely, together with some of the β-naphthol, as the *p*-nitrodiazobenzene compound. After 30 minutes the mixture is diluted with 60 c.c. of boiling water and filtered. The residue on the filter is washed with hot water, the washings being added to the filtrate. All the uncoupled β-naphthol will be in the filtrate, together with some of the azo-compound of the α-naphthol. The residue is washed off the filter and boiled with 50 c.c. of water containing 1 c.c. of 25 per cent. sodium hydroxide solution and the mixture filtered. The alkaline filtrate is diluted to 100 c.c. and the colour of the solution compared with that of a standard *p*-nitroazobenzene-α-naphthol prepared from pure α-naphthol. Since these colorations are fugitive, a secondary standard (*e.g.* Diamine Blue 2 B, *i.e.* tetrazotised benzidine coupled with " H " acid in a solution of sodium hydroxide) may be used.

Callan (*J.S.C.I.*, 1925, 126 T) found that the following modification of Prochazka's method is more sensitive to low concentrations of α-naphthol: 1·5 grms. of the sample are dissolved in 50 c.c. of methylated spirit, the solution cooled in ice and 10 c.c. of 0·05 *N* diazotised *para*nitroaniline added, with constant stirring. The mixture is allowed to stand for 30 minutes at a cool laboratory temperature and then diluted with 50 c.c. of boiling water, transferred to a porcelain dish and evaporated on the water-bath to a small volume to remove the alcohol. To the residue are added 50 c.c. of hot water, then 5 c.c. of 20 per cent. sodium hydroxide solution, and the mixture boiled gently for a few minutes, filtered whilst hot and the cooled filtrate and washings made up to 500 c.c. The depth of colour of this solution is compared with that of a standard solution prepared in a similar manner from 1·5 grms. of pure recrystallised β-naphthol to which a known amount of pure α-naphthol has been added. The α-naphthol is used in the form of a standard solution containing 0·15 grm. in 100 c.c. of alcohol.

CHAPTER XVIII.

THE DETECTION AND ANALYSIS OF DYESTUFFS.

The analysis of a dyestuff may have to be dealt with from several points of view. It may be necessary, for example, to determine

(1) whether it is a single dyestuff or a mixture of two or more dyestuffs ;
(2) the dyeing class to which it belongs ;
(3) its dyeing properties, such as tinctorial value, equalising power and rate of exhaustion of its solutions ;
(4) the impurities present ;
(5) the percentage of actual dyestuff present in the sample.

In addition to these, it is often desirable to find out the chemical nature of the dyestuff, *i.e.* the chemical class to which it belongs, or to ascertain what dyestuff has been used in dyeing a pattern which has to be matched.

Single Dyestuffs and Mixtures.

The following qualitative tests may be employed to differentiate single dyestuffs and mixtures :

(1) A little of the finely powdered sample is blown horizontally across the surface of a sheet of blotting paper moistened with water or methylated spirit. When the particles fall upon the surface of the paper they will produce coloured spots. When the sample consists of a single dyestuff each spot will have the same colour, but if two or more dyestuffs are present, differently coloured spots will generally be produced. Some concentrated sulphuric acid in a flat dish may be used instead of blotting paper or as a separate test. When a mixture of dyestuffs consists of perfectly homogeneous particles, this test fails.

(2) *The Capillary Test.*—A little of the dyestuff is dissolved in water and the solution placed in a flat dish. A thread of scoured cotton or a narrow strip of blotting paper is suspended vertically above the dish, the lower end of the thread or strip of blotting paper dipping beneath the surface of the liquid. The dye solution will rise gradually up the thread or paper. When only one dyestuff is present the colour of the wetted portion will be the same from top to bottom, but when a mixture is present the constituents will generally rise at different rates and zones of different colours will be obtained.

(3) *The Fractional Dyeing Test.*—A little of the dyestuff is dissolved in water and a dyebath is made up with the usual assistants for the class of dyestuff under examination. The contents of the bath are heated to the boiling-point and a small piece of cotton or woollen fabric about half an inch square is introduced. After a few minutes, when it has become fully dyed, the fabric is removed, the dye liquor squeezed from it into the bath and a second piece introduced, the process being continued until the dyebath is exhausted. When only a single dyestuff is present, every piece of fabric will be dyed the same colour, differing only in shade as the bath approaches exhaustion.

When a mixture of dyestuffs containing different colours is subjected to

the fractional dyeing test it will be found that, as a rule, the constituents have not the same affinity for the fabric, and that after exhausting the bath, the dyed patterns can be sorted out into two or more lots of distinctly different colours. If the dyestuff be stripped separately from each lot and the test repeated with the individual solutions obtained, a further separation is effected, the principle involved being similar to that of fractional crystallisation or fractional distillation.

When a mixture contains dyestuffs of the same colour these tests are inapplicable and the solution of the problem becomes extremely difficult, depending upon characteristics such as differing solubility in organic solvents. Naturally the components of a mixture belong as a rule to the same class. One would not, for example, mix an acid dyestuff with a basic dyestuff, nor a basic dyestuff with a direct dyestuff. The following chemical and physical methods of examination are often of assistance.

Separation by means of Organic Solvents.—The solubility of different members of the same class of dyestuffs in organic solvents is not always the same. Thus, some may be soluble and others insoluble in alcohol, others may be soluble in pyridine, amyl alcohol or amyl acetate. By extracting a dyestuff with various solvents a separation into its constituents may be effected. For example, Cochineal Scarlet G is only slightly soluble in alcohol, but Orange G dissolves freely. Hence a partial separation of these two bodies could be made by treating them with a limited amount of alcohol and filtering the mixture.

In the case of *acid dyestuffs*, the dye-acids which are carboxylated are soluble in ether, whilst the sulphonated dye-acids are insoluble in this solvent. Hence, if a solution containing acid dyestuffs be acidified with sulphuric acid and extracted with ether, any carboxylic acids present will be removed, the sulphonic acids remaining in solution. Some of the latter are moderately soluble in amyl alcohol and may be removed by means of this solvent; others form insoluble lead or silver salts and can be removed by precipitation. Acid dyestuffs differ from one another in another respect. Some of them are hydrolysed by water, others by a weak acid such as acetic acid, and the remainder only by strong acids such as hydrochloric or sulphuric acid. The members of the first class could be removed by taking advantage of the fact that they dye wool from a neutral bath. Those belonging to the second class also dye wool to a certain extent from a neutral bath, but require the presence of from 1 to 2 per cent. of acetic acid (on the weight of wool) to bring about exhaustion. The remainder do not dye wool in the absence of acetic acid, and sulphuric acid is required for exhaustion. Cain and Thorpe (*Synthetic Dyestuffs*, p. 378) classify acid dyestuffs as follows: (1) Those soluble in ether in neutral solution. (2) Those soluble in ether in the presence of 1 per cent. of acetic acid. (3) Those soluble in ether in the presence of hydrochloric or sulphuric acid. (4) Those insoluble in ether in the presence of acid.

The *basic dyestuffs* are all decomposed by alkalis with the liberation of the base. Dye-bases are generally soluble in ether. But the basic dyestuffs differ in the ease with which they are decomposed. They may, in fact, be classified as

(1) those which are hydrolysed by water;
(2) those hydrolysed by weak alkalis such as ammonia;
(3) those requiring a strong alkali such as sodium hydroxide to liberate the base.

Thus, by extracting an aqueous solution with ether and then repeating the extraction in the presence of ammonia and sodium hydroxide successively, a separation of the constituents may often be effected.

Separation by means of Adsorption.—Chapman and Siebold (*Analyst*, 1912, 339) showed that many dyestuffs are adsorbed completely from their aqueous solutions by finely powdered kaolin. A solution of 1 grm. of the dyestuff in one litre of water is made up and 10 c.c. of this solution are stirred for 5 minutes with 5 grms. of powdered kaolin previously made into a paste with a little water. The mixture is allowed to stand for 5 minutes and then filtered through a Gooch crucible by means of a pump. Dyestuffs may be divided into three classes, *viz.* : (1) those adsorbed completely, (2) those adsorbed incompletely, (3) those not adsorbed at all. Some dyestuffs which are soluble in alcohol and are adsorbed by kaolin cannot be recovered by washing the kaolin with alcohol.

Separation by means of Alkaloids.—It has been shown by Trotman and Frearson (*J. Soc. Dyers and Col.*, 1931, 344) that all direct dyestuffs are precipitated from their aqueous solutions by alkaloids. Some of the neutral-dyeing acid dyestuffs behave in the same manner, but most of the other acid dyestuffs either give no precipitate, or if they do, this precipitate is soluble in dilute acetic acid, whereas the alkaloidal compounds of direct dyestuffs do not dissolve. Separations of acid and direct dyestuffs or of ordinary and neutral-dyeing acid dyestuffs may be made by taking advantage of these facts.

Determination of the Class to which a Dyestuff Belongs.

When analysing an unknown dyestuff certain classes may be separated by treatment of the sample with water, in which sulphur dyestuffs, vat dyestuffs and most mordant dyestuffs are insoluble. Mordant dyestuffs which dissolve in water are generally bisulphite compounds, whilst a few of the solubilised vat dyestuffs are sulphonic esters.

About 1 grm. of the sample is made into a paste with a little cold water, hot water added, and the mixture boiled for a few minutes. After allowing to stand for a short time the liquid is decanted through a Gooch crucible. The undissolved residue left in the beaker is boiled again with water and the liquid decanted on to the filter as before, the process being repeated until no more colour is removed. The filter is now washed with hot water, and may be dried and weighed, or used as it is for qualitative tests. The insoluble matter may consist only of impurities. It is tested for dyestuffs in the following manner :

(*a*) **Sulphur Dyestuffs.**—All sulphur dyestuffs evolve *sulphuretted hydrogen* when heated with a suitable reducing agent, such as stannous chloride and hydrochloric acid. A little of the substance is placed in a small conical flask together with some stannous chloride and dilute hydrochloric acid. The flask is closed with a bung through which passes a small thistle funnel, the upper end of which is plugged with lead acetate impregnated cotton wool. It is heated gently on a water-bath or hot plate, and when a sulphur dyestuff is present a brown or black stain will be formed on the cotton wool.

(*b*) **Vat Dyestuffs.**—These do not give sulphuretted hydrogen in the stannous chloride test. They form *leuco-compounds* when treated with a reducing agent such as sodium hydrosulphite, these compounds being soluble in sodium hydroxide. A little of the insoluble residue from the water extraction is mixed with sodium hydroxide solution, a pinch of hydrosulphite added and the mixture allowed to stand. If a solution is formed, a vat dyestuff is present. The solution will be yellow or even colourless in the case of the *indigoid derivatives*, whilst the leuco-compounds of the *anthraquinone vat dyestuffs* often give coloured solutions. A spot of the leuco-solution is placed upon a piece of filter paper and exposed to the air. If it becomes coloured, an indigoid vat dyestuff is indicated. If no change of colour is observed, the spot is touched with a little

dilute solution of potassium persulphate. The leuco-compounds of anthraquinone derivatives will now be oxidised. Many of the vat dyestuffs can be sublimed by heating them carefully in a dry test-tube; indigoid vat dyestuffs are soluble also in pyridine and aniline. Green gives the following test: A little of the dyestuff or the insoluble residue obtained from the water extraction is boiled for two minutes with freshly distilled aniline and the extract, if coloured, is evaporated carefully to dryness in a test-tube. The dry aniline-free residue is heated carefully in a Bunsen flame, when, if an indigoid dyestuff be present, a coloured vapour will be produced.

Mordant Dyestuffs.—Two sample dyebaths are prepared containing water and a little of the dyestuff or insoluble residue from the water extraction. A piece of woollen fabric is placed in one bath and in the other a piece which has been mordanted with aluminium or chromium. The temperature of the dyebaths is now raised to the boiling-point. In the presence of a mordant dyestuff the unmordanted wool will merely be stained, whilst the mordanted piece will be dyed.

Examination of the Water-soluble Portion.—The filtrate obtained in the determination of insoluble matter may contain either acid, basic or direct dyestuffs. *Basic dyestuffs* may be identified first. A little of the solution is treated with a solution of tannic acid and sodium acetate; a suitable strength is 5 grms. of each dissolved in 100 c.c. of water. All basic dyestuffs give *insoluble tannates* in the absence of strong acids. A more delicate way of carrying out the test is to decompose some of the solution in a separating funnel with sodium hydroxide, then extract the liberated base with ether, evaporate the ether solution, dissolve the residue in dilute acetic acid and add the tannic acid to this solution. All basic dyestuffs dye cotton mordanted with tannic acid. Some bleached cotton is soaked in a warm solution of tannic acid for an hour. It is then squeezed and put into a cold dilute solution of antimony tartrate, after which it is washed well with water. This mordanted cotton is immersed in a little of the solution to be tested, made slightly acid with acetic acid. All basic dyestuffs dye tanned cotton from a cold or hot bath, whilst a piece of unmordanted cotton is not dyed, only stained.

If the presence of a basic dyestuff has been proved, *basic mordant* groups should be looked for. Some of the solution is heated with a solution of chromium fluoride containing sodium acetate (10 grms. chromium fluoride and 5 grms. sodium acetate in 100 c.c. water). Basic mordant dyestuffs give a precipitate.

When basic dyestuffs have been identified, acid or direct dyestuffs are not likely to be present. In the absence of basic dyestuffs they are tested for in the following manner: Two skeins of wool, one mordanted with potassium bichromate and the other unmordanted, and a piece of mercerised cotton, are placed in a boiling solution of the dyestuff containing a little acetic or sulphuric acid and sodium sulphate. If the wool is dyed and the mercerised cotton remains undyed, an *acid dyestuff* is probably present. If the colour of the mordanted skein of wool is deeper than or different from that of the unmordanted skein, the dyestuff is an *acid mordant colour*. This may be confirmed by boiling the dyed skeins with a one per cent. solution of ammonia. Most of the acid dyestuffs are stripped readily by ammonia, but the acid mordant colours are comparatively fast. Acid mordant dyestuffs give a precipitate when boiled with the chromium fluoride reagent.

Since *direct dyestuffs* generally dye wool from an acid dyebath, and since also the presence of acid tends to keep the colour off cotton, these tests are not in themselves conclusive. But the direct dyestuffs will dye cotton from a neutral or faintly alkaline bath containing salt or sodium sulphate. Small pieces of

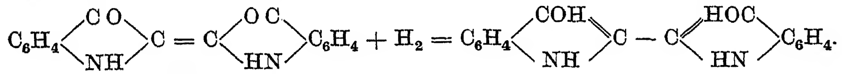
cotton or mercerised cotton are boiled in a solution of the dyestuff containing a little salt. The dyed sample is rinsed and boiled in a dilute solution of soap in water together with a fresh piece of mercerised cotton, and bleeding of the colour from the dyed to the undyed sample is looked for.

Green's Method of Analysis.

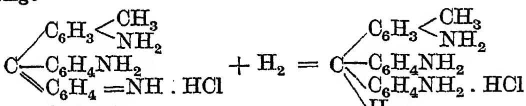
In a great many cases it is sufficient to know the group to which a dyestuff belongs, but some further information may be obtained by studying the action of *reducing agents*, particularly of zinc dust and acetic acid, upon it. This method was proposed originally by Green and is described fully in his *Analysis of Dyestuffs* (Griffin). When a dyestuff is subject to reducing action it may (1) remain unchanged, (2) become changed in colour, or (3) become decolorised. When changed in colour or decolorised the colour may be restored on oxidation, *i.e.* when reduction produces a leuco-compound. When, however, a dyestuff is an azo-compound, or contains nitro- or nitroso-groups, it is changed into one or more new substances on reduction, which cannot reproduce the dyestuff when oxidised. Thus *nitro-compounds* and *nitroso-compounds* are changed into *amines* and *azo-compounds* into a mixture of two or more *amines*. For example, Orange IV gives aminoazobenzene and sulphanilic acid, thus :

$$C_6H_4\left<\begin{matrix} N:NC_6H_4N:NC_6H_5 \\ SO_3H \end{matrix}\right. + 4\,H = C_6H_4\left<\begin{matrix} NH_2 \\ SO_3H \end{matrix}\right. + H_2NC_6H_4N:NC_6H_5.$$

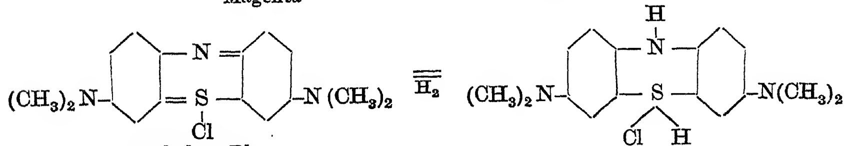
True *leuco-compounds* are illustrated by Indigo, Magenta and Methylene Blue, which react with hydrogen in the manner shown in the following equations :



Indigo



Magenta



Methylene Blue

These facts were made use of by Weingärtner and developed by Green into a detailed method of analysis.

The dyestuffs are grouped first into four classes, viz. :

(1) Basic and basic mordant dyestuffs, precipitated by tannic acid.

(2) Salt (direct) and sulphur dyestuffs, not precipitated by tannic acid, but dyeing unmordanted cotton.

(3) Acid and acid mordant dyestuffs, not precipitated by tannic acid, and without affinity for unmordanted cotton.

(4) Insoluble sulphide, mordant, pigment, spirit and vat dyestuffs insoluble in water.

These classes are identified by the special tests already described. When this has been done, the dyestuff is reduced with zinc dust and acetic acid. Some hot solution of the dyestuff is placed in a test-tube and sufficient zinc dust to cover the tip of a penknife is added. The mixture is agitated and then a five per cent. solution of acetic acid is added drop by drop until decolorisation occurs or it is established that no reduction takes place. The solution is decanted from the excess of zinc dust on to a piece of white filter paper which is exposed to the air. If after about two minutes no colour is produced, the paper is touched with a glass rod dipped in an acid solution of potasssium permanganate (1 grm. potassium permanganate and 2 grms. sulphuric acid per litre). Warming gently over a flame accelerates oxidation. In the case of red acid dyestuffs, which do not give their true colours whilst acid, the paper, after spotting with permanganate, is held over a bottle of strong ammonia.

The behaviour of different types of dyestuffs towards this test is shown in the following table:

Decolorised by Zinc Dust.			Unaltered by Zinc Dust or only Slowly and Partially.	Not Decolorised but Changed in Shade Completely.
Colour Restored by Air.	Colour Restored by Oxidising Agents.	Colour Not Restored by Air or Oxidising Agents.		
Azines. Oxazines. Thiazines. Indigoids. Pyrones (violet, blue). Acridines.	Triphenyl-methane Dyes. Pyrones (red). Anthraquinone Vat Dyes.	Nitro-, Nitroso- and Azo-Dyes.	Quinolines. Thiazols.	Anthracene Dyes.

The results of the reduction test indicate the type of dyestuff, and this is sufficient for many purposes. When further information is required, special colour reactions are made use of, the results of which have been tabulated for a large number of dyestuffs. It is better to apply these tests to either wool or cotton dyed with the dyestuff. These tables are given in Green's book referred to already. It may be noted that even with the aid of tables it is, in a great many cases, impossible to identify a particular dyestuff with any degree of certainty. If there were only a few dyestuffs which could be used, their identification would not be difficult, but with several thousands to choose from, the problem becomes extremely complex. As a rule, however, when a practical dyer knows the group to which a dyestuff belongs, he has the information necessary to enable him to match a pattern.

The Identification of Dyestuffs on Dyed Fabrics.—The principles of the methods used are the same as for the dyestuffs themselves, except that, according to Green's method, a formaldehyde compound of sodium sulphoxylate is used as the reducing agent and potassium persulphate as the oxidising agent. These solutions are made as follows:

Hydrosulphite B (for yellow and orange colours): 50 grms. of Hydrosulphite NF concentrated, Hyraldite C extra or Rongalite C, are dissolved in 500 c.c. of water and acidified with 2 c.c. of acetic acid.

Hydrosulphite AX.—50 grms. of Hydrosulphite NF concentrated or Rongalite C are dissolved in 150 c.c. of hot water. To the hot solution (at 80°–90° C.) is added 0·25 grm. of anthraquinone ground to a fine paste with a little of the

solution, and the whole is diluted to 500 c.c. with cold water. The solution should always be slightly alkaline to litmus paper.

Persulphate.—A cold saturated aqueous solution of potassium persulphate is used, or a one per cent. solution of ammonium persulphate, neutralised, if alkaline, with dilute acetic acid.

The reactions are carried out in test-tubes with pieces of the dyed material $\frac{1}{2}$ to $\frac{3}{4}$ in. square. The sample is boiled for from one-quarter to one minute with the hydrosulphite, then rinsed thoroughly under the tap and allowed to lie on white paper for an hour or so. The colour generally returns either immediately or in a few minutes in the case of air-oxidisable leuco-compounds, but the action may be accelerated by exposing the pattern to ammonia. If the colour does not return on exposure to air, the pattern is heated to the boiling-point in a test-tube with a little water and potassium persulphate solution is added drop by drop, avoiding an excess. If still no colour returns, the dyestuff may be regarded as an azo-, nitro- or nitroso-compound, or an azoic colour.

As a rule, when determining the nature of a dyestuff used for dyeing a pattern, valuable information can be obtained from preliminary tests. Thus, if a mordant be found, the examination is simplified, although the mordant dyestuffs are used in conjunction with others. *Logwood* can be detected easily by boiling the sample with 5 per cent. hydrochloric acid, when a red or crimson solution is obtained which is changed to violet by adding excess of alkali. *Sulphur dyestuffs* are detected by the test already described, and *vat dyes* by dissolving them in alkaline hydrosulphite solution and exposure of the solution, spotted on filter paper, to air, or treating the paper with potassium persulphate. *Indigoid colours* can be sublimed by heating a piece of the sample in a dry test-tube.

Aniline Black may be identified by the following tests: A piece of the sample is soaked in cold concentrated sulphuric acid until it has dissolved. The solution is poured into cold water, when a greenish-black precipitate or a pale green solution is produced. When Aniline Black is treated with a solution of bleaching powder (2° Tw.), it becomes brown, whilst *Sulphur Blacks* are decolorised. *Paranitroaniline Red* and some other similar azoic colours are sublimed by heating, and are often extracted by boiling pyridine.

After making preliminary tests the following method may be adopted:

(1) The pattern is boiled with a one per cent. solution of acetic acid to extract basic dyestuffs. The solution obtained is tested with tannic acid or tanned cotton, as in the case of dyestuffs themselves, and mordant groups identified by means of the chromium fluoride reagent.

(2) The sample is now boiled with 1 per cent. solution of ammonia. Both acid and direct dyestuffs will be removed readily, but acid mordant dyestuffs only slowly. The ammoniacal solution is divided into two parts. One part is acidified and boiled with some wool and mercerised cotton; the other portion is boiled until most of the ammonia has been expelled, a little salt then added and some wool and mercerised cotton. From the results given by these two tests the nature of the dyestuffs can be ascertained as already described. When an acid dyestuff has been identified it should be tested for mordant groups in the manner just described.

The mordant dyestuffs, azoic colours, vat dyes and sulphur dyestuffs will still remain, and are identified by the special tests already given.

The differentiation between indigoids and indigosols may be effected by *Livingston's test* (*Bull. Soc. Ind. Mulhouse*, 1929, **95**, 230): The pattern is stripped with an alcoholic solution of sodium hydrosulphite, boiled in a 0·025 per cent. solution of Methylene Blue, washed and dried. Fabric dyed with an

indigosol has a definite affinity for the basic dyestuff, whereas fabric dyed in the vat has not. This affinity for Methylene Blue is independent of the method of developing the indigosol, and is not due to the presence in the fabric of oxycellulose ; it is suggested that the sulphuric acid formed by hydrolysis of the indigosol simultaneously combines with the cotton, thereby conferring on it an affinity for the basic dye.

Detection of Mordants.

The ash of textile fibres rarely exceeds one per cent. and is generally white or grey in colour. A high ash, especially if coloured, will indicate the presence of a mordant, and usually the appearance and colour will give sufficient indication of the nature of the mordant present. The following table indicates this.

Mordant.	Compound in Ash.	Colour of Ash.
Chromium, . . .	Cr_2O_3	Green.
Copper, . . .	CuO	Black.
Iron, ...	Fe_2O_3	Reddish-brown.
Aluminium, . . .	Al_2O_3	White and bulky.
Tin, ...	SnO_2	Yellow hot, white cold.

When an acid mordant dyestuff has been used there is not always sufficient chromium oxide present to give the ash a green colour. The borax bead test may then be used, or the ash may be mixed with magnesia and ignited to convert the chromium into chromate. The ash is extracted with water and filtered and the filtrate tested for chromate by adding a crystal of potassium iodide and acidifying with dilute hydrochloric acid ; iodine will be liberated if chromate is present and may be identified by means of starch solution.

Azo-dyestuffs.

The examination of azo-dyestuffs is facilitated greatly if the products of reduction can be isolated and identified. The following simple example will illustrate this : When Orange IV is reduced, sulphanilic acid and aminoazobenzene are formed. If the mixture be made alkaline and extracted with ether the latter compound is separated ; it can then be recrystallised from alcohol and its melting-point, 127° C., determined. The solution of the sulphanilic acid may be diazotised and coupled with dimethylaniline hydrochloride, when methyl orange is formed in accordance with the equation

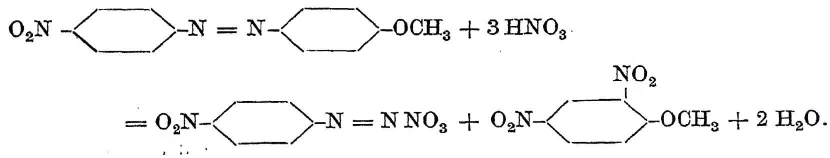
$$C_6H_4\left\langle\begin{matrix}N:NCl\\ SO_3H\end{matrix}\right. + C_6H_5N(CH_3)_2 = C_6H_4\left\langle\begin{matrix}N:NC_6H_4N(CH_3)_2\\ SO_3H\end{matrix}\right. + HCl.$$

This method was used first by Green and has been improved by Rowe and Levin, Forster and Hanson, Schmidt, and others.

In Green's process (*Analysis of Dyestuffs*, p. 109) the dyestuff is decomposed by a suitable reducing agent such as sodium hydrosulphite, zinc dust or stannous chloride. Amino-derivatives of second components, such as aminonaphthols and their sulphonic acids, usually separate at once from the hot solution, or upon cooling, or in some cases when the solution is saturated with salt or mixed with a large excess of concentrated hydrochloric acid. After removing these bodies

the liquid is made alkaline and distilled or extracted with ether. When volatile bases are present, such as aniline, toluidine, etc., they can be isolated readily and identified by their boiling-points or other properties. Non-volatile bases are extracted with ether and purified by distillation or crystallisation of the hydrochlorides or sulphates. A method depending on nitration is described also: The dyestuff (freed from salt) is added slowly to 10 to 20 times its weight of red fuming nitric acid which is kept cooled to 20°–30° C. After standing for about ten minutes the colour of the solution will have changed to brownish-yellow, and the mixture is poured on to chopped ice. According to the nature of the dyestuff, either the diazo-compound or the nitrophenol, more usually the latter, may be sparingly soluble in water and separate out. If both products are insoluble, the nitrophenol is separated from the diazo-compound by extracting the precipitate with alcohol, ether or benzene. If both products are soluble the nitrophenol, if unsulphonated, may be extracted with ether, leaving the diazo-compound in solution, or the latter may be removed by coupling it with β-naphthol. The diazo-compound is identified by coupling it with β-naphthol or "R"-salt and reducing the product, the nitrophenol by its melting-point or other properties. The aminosulphonic acids, which are the chief intermediates used, do not possess definite melting-points; Green identified them by dissolving them in ammonia and spotting the ammoniacal solution on filter paper, when in most cases a colour reaction is obtained.

Rowe and Levin (*J. Soc. Dyers and Col.*, 1924, 218) and Forster and Hanson (*J. Soc. Dyers and Col.*, 1926, 272) have improved Green's method and have published details of a large number of reduction products. Schmidt (*Ber.*, 1905, 38, 3201) found that when an azo-compound is nitrated the diazonium compound used in the preparation of the azo-compound is recovered as a rule in the form of its nitrate, whilst the coupling component is obtained as a nitro-derivative, thus:



The diazonium nitrate and the nitro-compound are separated readily by suitable means, and the latter can be identified from its melting-point, etc. Rowe and Levin couple the diazonium nitrate with β-naphthol or Naphthol AS. The resulting azo-compounds have well-defined melting-points, and consequently the diazo-component used in their preparation can be identified. Tables of melting-points, crystalline structure and colour reactions are given by the investigators.

For the reduction process Forster and Hanson use either stannous chloride or hydrosulphite, the former being most suitable for obtaining an azo-compound of the naphthalene or benzene series containing an acid group. The dyes in which the azo-component is a phenol or amino-compound of the benzene series are best reduced with hydrosulphite. The acid stannous chloride solution is made by dissolving 40 grms. of stannous chloride in 100 c.c. of concentrated hydrochloric acid. About 75 c.c. of this solution are heated to the boiling-point and about 1/20 gramme-molecule of finely powdered dyestuff is added in small portions to the boiling solution, a subsequent portion being added only when the

preceding one has been decolorised. When all the dye has been added and reduced, the reduced mixture is boiled for a few minutes, after which the sides of the beaker are washed down with a little water and the whole allowed to cool. In some cases the amino-derivative separates from the hot solution ; in others only on standing. The precipitate is filtered off at the pump ; the bulk of the stannous chloride and diazo-components remain in the filtrate, but some of the latter are found in the precipitate and are removed in the following manner: When the precipitate is sparingly soluble in water or alcohol, it is washed with from 100 to 150 c.c. of cold water and then with the same volume of alcohol. It is then macerated with alcohol and again filtered. When the precipitate is soluble in water, only alcohol is used. If it be soluble in alcohol and sparingly soluble in water it is washed with the latter and then recrystallised from alcohol. When the precipitate is soluble in both water and alcohol it is purified best by recrystallisation once or twice from alcohol. The washing with or recrystallisation from alcohol removes the last traces of stannous chloride, the hydrochlorides of the amino-compounds and water. Even traces of water cause darkening of the product on drying. Hydrosulphite is used in the following way : A small portion of the dye is added to about 100 c.c. of boiling water and when dissolved, a small quantity of hydrosulphite solution is added and boiling continued until the liquid is decolorised, the operation being repeated until the whole of the dye has been added and reduced. If the free bases produced by reduction are volatile, the reduction flask must be provided with a reflux or inclined condenser ; the latter is recommended by Forster and Hanson, since it enables the volatile and non-volatile compounds to be separated. The non-volatile bases are extracted with benzene, but since many are soluble in water the ordinary method of shaking in a separating funnel is not suitable; the reduction mixture may be evaporated to a small volume in a fairly large flask and then boiled in the same flask with benzene. A more satisfactory method is to use a continuous extractor, in which case no concentration of the reduction mixture is necessary. Aminophenols will be present as sodium salts after reduction with the hydrosulphite ; these compounds are decomposed by passing carbon dioxide through the mixture before extraction.

Some insoluble azo-dyestuffs are not reduced by the methods described. In these cases the dye is dissolved in a suitable solvent such as alcohol before reduction. The reducing solution is placed in a distilling flask and the solution of the dyestuff allowed to run into the boiling reducing solution gradually through a tap funnel. The distilling flask is connected to an inclined condenser which permits the separation of the excess of alcohol and volatile reduction products. If preferred, the reducing solution may be added to the alcohol solution of the dyestuff.

The amino-compounds having been separated, 0·1 grm. is dissolved or suspended in 10 c.c. of water and 1 c.c. of concentrated ammonia. The contents of the tube are shaken and any colour change noted. A portion of the solution is poured on to filter paper, any change of colour noted and the moist stain on the paper treated with various reagents. A second portion of the ammoniacal solution is dried on filter paper for three minutes at 80° C. in a water oven and the dry residue treated with the following spotting agents : (1) Vanadium chloride (1 per cent.) ; (2) Schweitzer's solution, made by dissolving 5 grms. of copper sulphate in 100 c.c. of water and adding sufficient ammonia to dissolve the precipitate formed ; (3) five per cent. solutions of hydrochloric acid, ferric chloride, potassium bichromate, nickel chloride, uranium sulphate, potassium ferrocyanide, potassium ferricyanide, ferrous ammonium sulphate, cobalt nitrate and silver nitrate.

The General Analysis of Dyestuffs.

Commercial dyestuffs may contain various impurities, either added as diluents or not removed completely during manufacture. These include *sulphates*, *chlorides*, *carbonates*, and *organic matter* other than dyestuff. The detection and determination of these does not present much difficulty. *Sulphates* are determined in the usual manner by means of barium chloride. Voteck's method is generally suitable for the determination of *chlorides*. Bohanes (*J.S.C.I.*, 1927, B 211) determines (*a*) *water-insoluble matter*, (*b*) *ash*, (*c*) *soluble salts* by dialysis, (*d*) *chlorides*. When a dyestuff is soluble in an organic solvent this should be used in preference to water for determining *insoluble matter*, since in this case the residue will indicate organic as well as inorganic impurities. Sometimes it is useful to precipitate the dyestuff by means of sodium chloride ; *sulphates*, for example, can be determined in the filtrate. Both acid and direct dyestuffs can be treated in this way, whilst basic dyestuffs can, as a rule, be dissolved in alcohol.

Carbonates may be detected and determined by Hepburn's method (*Analyst*, 1926, 622): A filter flask of 750 c.c. capacity, fig. 57, is used. A tap funnel (B) passes through the rubber bung, the lower end being just above the opening of a tube (C) which contains from 0·15 to 0·3 grm. of the dyestuff. The filter flask contains 50 c.c. of normal barium hydroxide solution. Dilute (3 *N*) hydrochloric acid, free from carbon dioxide, is placed in the tap funnel. The flask is connected to a vacuum pump and evacuated to a pressure of 2 cm. of mercury. The clip E is then closed and the acid added cautiously drop by drop until no further effervescence occurs. The flask is then allowed to stand for about 12 hours and the unused barium hydroxide determined by titration with normal oxalic acid in the presence of phenolphthalein.

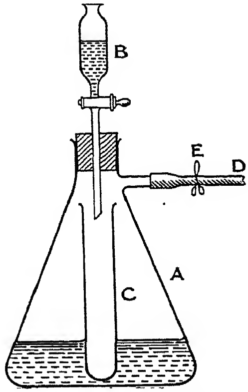


Fig. 57.—Hepburn's Apparatus.

The determination of *nitrogen* is sometimes useful. The ordinary Kjeldahl method cannot be used when azo-, nitro- or nitroso-groups are present. These groups must first be reduced by Jodlbauer's method, described in Chapter V. Sisley and David (*Bull. Soc. Chim.*, 1929, **45**, 312) state that the following modification gives accurate results except in the case of pyrazolones: The substance (0·5–1 grm.) is warmed in a 250 c.c. Pyrex flask with 10 c.c. of alcohol and 5 c.c. of water, 2–4 grms. of sodium thiosulphate are added, 1 grm. at a time and with boiling and cooling after each addition, followed by 10 c.c. of sulphuric acid, density 1·84, and the flask gently heated to expel alcohol ; when the liquid becomes spongy 0·5 grm. of copper sulphate, 6–8 grms. of potassium sulphate (10 grms. less the weight of thiosulphate used) and 12 c.c. of sulphuric acid are added. The mixture is heated until the liquid is clear blue (20–30 mins.), diluted to 300 c.c., and the ammonia determined as usual, 5 c.c. of 20 per cent. sodium sulphide solution and a little granulated zinc being added with the sodium hydroxide before distillation.

For the detection or determination of metals, such as *lead*, *copper* or *chromium*, the ash may be used, but it is better as a rule to destroy organic matter by the Kjeldahl process. A weighed quantity of the dyestuff is heated with sulphuric acid in a large Kjeldahl flask until solution is effected. The

contents of the flask are then cooled, some potassium sulphate and a little perchloric acid added and heating continued until a colourless solution is produced. A second or third addition of perchloric acid may be necessary. When oxidation is complete the contents of the flask are cooled and diluted with water. Lead sulphate, if present, will be precipitated and is filtered off on a Gooch crucible, washed with one per cent. sulphuric acid, dried, ignited at a low temperature and weighed. The remaining metals can be separated from the filtrate in the ordinary manner.

The Determination of Dyestuffs.

There is no general method applicable to the determination of dyestuffs owing to their varied and complex nature. Many methods have been proposed, which may be grouped as follows:

(1) Special methods applicable to particular dyestuffs.
(2) The titration of one dyestuff with a standard solution of another with which it forms an insoluble compound.
(3) Alkaloidal precipitation.
(4) Titration by means of a standard solution of titanous chloride.

Special Methods.—The determination of *Indigo* by *Green's method* is a good example. It depends upon the fact that indigo, when treated with sulphuric acid under suitable conditions, yields a disulphonic acid which may be determined by titration with decinormal potassium permanganate solution. The method may be applied either to the analysis of Indigo itself or to the determination of the dye on a dyed fabric. The sample is dried and extracted with boiling pyridine in a continuous extractor until no more colour is removed. The solution is cooled, when most of the dissolved Indigo crystallises out. The remainder is precipitated by adding about 100 c.c. of 50 per cent. alcohol. The precipitate is filtered off on a weighed Gooch crucible and washed successively with (1) hot 50 per cent. alcohol, (2) hot 2 per cent. sodium hydroxide solution, (3) hot 1 per cent. hydrochloric acid, (4) hot water, (5) alcohol, (6) ether. This treatment will remove all dyestuffs other than Indigo. The crucible is dried at 110° C. and weighed. The precipitate may then be converted into the disulphonic acid by transferring the crucible to a small beaker containing 15 to 20 c.c. of pure sulphuric acid and warming for 45 minutes at a temperature of 70°–80° C. The solution is then washed into a 500 c.c. flask, cooled and made up to the mark with distilled water. An aliquot part is diluted largely with water and titrated with $N/50$ potassium permanganate solution; each cubic centimetre used corresponds to 0·0015 grm. of Indigo.

Noll (*J. Soc. Dyers and Col.*, 1927, 33) gives the following method for determining *indigosols*: From 0·5 grm. to 1 grm. of the dyestuff is dissolved in 100 c.c. of water and the solution filtered. The filtrate is acidified with sulphuric acid and warmed. Sodium nitrite is then added until the Indigo or tetrabromindigotin has separated completely. The precipitate is filtered off on a Gooch crucible, washed, dried at 100° C. and weighed. The same author describes a special method which is applicable to *Auramine*. When this is boiled for 15 minutes with equal volumes of concentrated hydrochloric acid and water, it is decomposed quantitatively into ammonium chloride and a ketone. Auramine O gives $p:p'$-tetramethyldiaminobenzophenone (melting-point 173° C.) and Auramine G gives *o*-dimethyldiaminoditolyl ketone (melting-point 80° C. to 81° C.).

Another interesting example of a special method is the determination of *Methylene Blue* by precipitation with picric acid, due to François and Sequin (*J. Pharm. Chim.*, 1929, **10,** 5-9): 1 grm. of Methylene Blue is weighed out carefully, placed in a 100 c.c. flask, dissolved in water and the solution diluted to 100 c.c. 10 c.c. of the solution (which contain 0·1 grm. of Methylene Blue) are placed in a 125 c.c. conical flask and 20 c.c. of an aqueous solution (5 grms. per litre) of picric acid are added. Immediately a purple-black precipitate is formed and leaves a clear yellow solution. After filtration the precipitate is carefully washed with 10 c.c. of water to remove any excess of picric acid, pressed lightly between filter papers, then left to dry (either in the air or in a desiccator over sulphuric acid), and weighed. The crystalline *picrate* which is precipitated is formed of one molecule of Methylene Blue and one molecule of picric acid with no water of crystallisation. The molecular weight of picric acid is 229, that of Methylene Blue 373·5 (with 3 molecules of water), or 319·5 (anhydrous), hence the molecular weight of the picrate is 548·5. Therefore to obtain the weight of Methylene Blue, the weight of the dry precipitate is multiplied by $\frac{373 \cdot 5}{548 \cdot 5}$, or 0·6809.

Trotman and Frearson (*J. Soc. Dyers and Col.*, 1931, 346) showed that *basic dyestuffs* are precipitated by silicotungstic acid from solutions made slightly acid with hydrochloric acid. If precipitation is carried out at the boiling point, the precipitate settles quickly. The clear liquid is decanted through a weighed Gooch crucible. The precipitate is washed three times in the beaker with boiling water containing a little hydrochloric acid. It is finally transferred to the Gooch crucible, washed with hot water, dried and weighed. It is then heated until a residue of $SiO_2.12WO_3$ is obtained, cooled and weighed. The difference between the two weights gives the basic dyestuffs present.

A method of determining *sulphur dyestuffs* (Touschof-Vtosov, *Rev. Ind. Tex.*) is as follows: 0·1–0·5 grm. of the sulphur dyestuff, according to its strength, is dissolved with sulphide of soda and eight to ten times its weight of water in a glass beaker of capacity 300–400 c.c.; a solution of a basic colour, for instance Safranine (0·5 grm. per litre), is run in from a graduated burette until the precipitate falls to the bottom of the beaker (5–10 minutes), and the liquid becomes quite clear and acquires a slight pink coloration. If an insufficient amount of the basic colour solution has been added the precipitate does not fall quickly enough. The precipitate obtained is collected in a tared filter and dried to a constant weight, then washed first with cold water, then hot water, until the wash water ceases to react with silver nitrate. It is then washed with glacial acetic acid and finally with a mixture of glacial acetic acid and alcohol, which dissolves the leuco-compound of Safranine formed in the alkaline medium. The precipitate is then dried and weighed.

Determination by Titration with Another Dyestuff.—Strongly *acid* and strongly *basic* dyestuffs precipitate each other in dilute aqueous solution; those with weakly acid or basic properties precipitate only a limited number of dyestuffs of the opposite properties, depending upon the degree to which the acid or basic character of the precipitant predominates. Brown and Jordan (*J. Soc. Dyers and Col.*, 1923, 203) found that (1) the dyestuff to be estimated and the volumetric reagent selected must have, when in solution, quite different colours, *e.g.* blue and yellow; (2) the acid colour should be run into the solution of the basic dyestuff, the reverse process seldom giving a good result; (3) a quick decision must be made in determining the end-point. The solutions used should contain 1 grm. per litre and the end-point is recognised by the appearance in a spot made on filter paper of a ring with the colour of the precipitating solution.

In some cases where the end-point is not very definite, a mixed solution of the dyestuff and tannic acid can be employed since the precipitate formed in the presence of this acid is more granular and settles more quickly. For example, *Brilliant Green* and *Malachite Green* are titrated with a solution of *Orange II* containing 1 grm. of the dyestuff, 2 grms. of tannic acid and 2·5 grms. of sodium acetate per litre, 25 c.c. of the Green solution being titrated until no further precipitate is formed, this point being indicated by the appearance of an orange ring on the filter paper. *Magenta* is treated in the same way. The following are further examples of suitable pairs of dyestuffs :

Auramine and Indigo Carmine.
Methyl Violet and Naphthol Yellow.
Rhodamine B and 6 G and Metanil Yellow + tannic acid.
Safranine and Tartrazine.

Direct dyestuffs may be titrated directly with suitable *basic dyestuffs*, but in many cases it is better to add an excess of the basic dyestuff solution and titrate-back with a suitable acid dyestuff. Thus *Benzopurpurin* and *Chrysophenine* are treated with an excess of a standard solution of *Auramine* and the residual basic dye determined by titration with *Orange II*. Naturally only pure dyestuffs must be used for the standard solutions, and these solutions must be standardised against each other.

Determination of Direct Dyestuffs by Precipitation with Alkaloids.—Trotman and Frearson (*loc. cit.*) found that the precipitate produced by adding excess of a solution of an alkaloidal salt to one containing a direct dyestuff has the composition represented by the formula $(RSO_3H)_2A_2$, where RSO_3H is the dye acid and A the alkaloid. These precipitates can be filtered on a Gooch crucible, washed with a cold saturated aqueous solution of the alkaloidal salt, dried and weighed.

Titration with Titanous Chloride Solution.—This method, which was proposed by Knecht (*New Methods in Volumetric Analysis*), can be used for every dyestuff which forms a *leuco-compound* or is decolorised by reduction. The preparation and method of application of the titanous chloride solution has been described in Chapter IV. Many dyestuffs can be titrated directly, but in other cases excess of the titanous chloride solution is added and the unused portion determined by back-titration with standard ferric alum solution. Sometimes the presence of Rochelle salt or sodium tartrate is necessary for the formation of the leuco-compound. The following examples are taken from Knecht's book :

(*a*) *Methylene Blue.*—Dissolve 1 grm. of the dyestuff in 250 c.c. of water, place 50 c.c. of this solution in the titration flask and add a little hydrochloric acid. Pass carbon dioxide through the solution and heat the contents of the flask over a Bunsen burner. Then run in the titanous chloride solution until the colour just disappears. From the equation

$$C_{16}H_{18}N_3SCl + H_2 = C_{16}H_{20}N_3SCl$$

it is evident that 319·5 parts of Methylene Blue are equivalent to 112 parts of iron.

(*b*) *Magenta.*—50 c.c. of a solution of 1 grm. of the dyestuff in 500 c.c. of water are placed in the flask with 25 c.c. of a 20 per cent. solution of Rochelle salt. The mixture is boiled and titrated as before in the presence of carbon dioxide.

(*c*) *Benzopurpurin* on dyed cotton. A weighed quantity of the sample is placed in the titration flask and boiled with dilute hydrochloric acid. Carbon dioxide is then passed in and an excess of the titanous chloride solution is added.

The flask is heated until the colour of the dyestuff has disappeared. It is then cooled and the excess of titanous chloride is titrated with standard iron alum solution, using potassium sulphocyanide as indicator. One part of Benzopurpurin 4 B is equivalent to 0·618 part of iron.

Comparative Dyeing Values of Two Dyestuffs.

Solutions of the two dyestuffs of identical concentration are made up. Two dyebaths are prepared containing the same quantities of dyestuff solution, assistants and water. A skein of wool or other material is dyed in each bath under identical conditions and each skein being of the same weight. After dyeing, the excess of dye liquor is squeezed back into the bath and the skeins are washed, dried and compared. If one is lighter in colour than the other it is put back into its own dyebath, a small measured volume of the dyestuff added and dyeing continued, followed by re-examination of the skein. Still more of the dye solution is added, if necessary, until the two skeins match one another exactly. The weights of the two dyestuffs required to give identical shades are calculated. These weights vary inversely with the dyeing values of the two dyestuffs.

Comparative Exhausting Powers of Two Dyestuffs.

Two wide-necked flasks are marked to indicate a convenient volume, *e.g.* 250 c.c. In each are placed the same quantities of dyestuff and assistants and the volumes made up to 250 c.c. Skeins of wool of the same weight are dyed, one in each flask under identical conditions. The skeins are removed, the excess of dye liquor squeezed back into the flasks and the volume of the liquids made up to 250 c.c. with water. Two more skeins are now dyed, and the operation repeated until no more dyestuff is taken up or until the dye liquors become colourless. The comparative exhausting powers will vary inversely with the weight of wool used.

Determination of Levelling Power.

A piece of fabric is tied together tightly in one place and dyed under the usual conditions until much of the dyestuff has been taken up. The tied portion is then undone and the fabric put back into the bath. If the dyestuff has good levelling power the previously bound portion will now be dyed to the same shade as the rest of the sample.

Determination of Tinctorial Value.

The tinctorial values of dyestuffs of the same colour may be compared by making solutions of a definite concentration and finding what volume of the solution with the stronger colour is required to match the colour of the other solution. The test is carried out in graduated cylinders.

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